Microkinetic Modeling of the Transient CO₂ Methanation with DFT-Based Uncertainties in a Berty Reactor

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The transient operation of methanation reactors can become desirable when coupled with fluctuating renewable energies in Power-to-Gas scenarios, which requires suitable kinetic approaches that can describe the transient catalytic phenomena. A combined experimental and theoretical investigation of the transient CO₂ methanation is conducted using concentration forcing to derive a suitable microkinetic model. Methanation experiments are performed with a Ni/SiO₂ catalyst in a Berty-type reactor at industrially relevant conditions. The microkinetic approaches are required that can accurately quantify the transient phenomena on the catalyst surface.[1]

One prominent and important example is the hydrogenation of CH₄ to CH₃OH in the Power-to-Gas (PtG) process.[2,3] Methanation reactors have primarily been designed for and operated in a steady state.[4] During transient operation, substantial temperature and concentration gradients can occur inside the packed-bed reactors,[5,6] which cause harm to the process through, e.g., deactivation of the catalyst.[4] Therefore, it is essential to predict how the reactor and catalyst behave under transient conditions, which is an interplay of the dynamic catalytic processes and the transport phenomena,[7,8] through sophisticated modeling. Such a model can also be used to control the reactor (i.e. digital twin) and to optimize the performance for desired product gas qualities. Foremost, for the model to be predictive, suitable kinetic approaches are required that can accurately quantify the transient phenomena on the catalyst surface.[1]

Transient operation in the PtG process can occur as a result of chaotic fluctuations in the feed concentration, which a forced periodic concentration modulation can approximate. One form of this operation is the alternation of the feed between two gas mixtures, also known as the “bang-bang” operation.[9] This mode has previously also been applied for the CO₂[10–13] and CO₂ methanation[14–18] to investigate the possibility of a process improvement through a dynamic operation. Additionally, the concentration forcing is also a valuable tool for the kinetic investigation of the reaction since adsorption/desorption steps become visible during the transients and the evolution of intermediates on the catalyst surface can be observed.[19–21]

Many studies have investigated the reactor behavior during the dynamic operation through reactor modeling and all of them have used global rate expressions such as the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach.[22–26] However, the parameters of these kinetics are always regressed to steady-state experiments.[19–21] Although these kinetic approaches are used frequently, they fail to accurately describe transient effects commonly observed in methanation experiments. Among these are chromatographic effects,[14,16,34] storage of adsorbates on the surface,[15,18,35,36] or overshoot in concentrations during back-transients.[14,17,18] A detailed description of all phenomena can be achieved in principle through rigorous microkinetic modeling, where all elementary steps on the catalyst surface are considered. There have been attempts in the past to use simplified transient kinetics, which account for adsorption/desorption and storage on the catalyst while lumping together the surface elementary steps.[16] These approaches are limited in their usage since the parameters are regressed to experiments, which can lead to wrong predictions outside the regressed range.[17] Moreover, microkinetic models can be easily used with efficient algorithms in typical reactor models using the mean-field approximation.[18–40] The main
challenge in microkinetic modeling is the mechanism construction and parametrization of all energetic parameters.

Microkinetic models for the CO₂ methanation reported in the literature are either based on first-principles[41–43] or semi-empirical estimation routines.[44–46] The semi-empirical microkinetics have been derived for Ni/Al₂O₃ catalysts[44–46] since they are the catalyst of choice when it comes to activity and selectivity.[47] However, the Al₂O₃ support interacts strongly with CO₂ and can also provide active sites on the support or metal/support interface,[48,49] which overshadows the kinetics of the Ni crystal. A more predictive description of the transient processes can be achieved by first-principles-based microkinetics, where a specific Ni facet is investigated.[41,42] Yet, the problem in first-principles-based microkinetic development is the uncertainty in energetic parameters caused by the approximations in the treatment of the electron correlation and exchange in the DFT code, which leads to error bars of 20–30 kJ mol⁻¹.[40,50–52] At the moment, there is no microkinetic model available that has been rigorously tested for the transient methanation of CO₂ on either single Ni facets or supported Ni catalyst.

We aim to close this gap by providing a microkinetic model derived from first principles via an automated mechanism generation procedure that has been thoroughly compared with dynamic methanation experiments. Forced periodic operation was used to investigate the dynamic methanation on a Ni/SiO₂ catalyst in a Berty-type reactor over a broad temperature (275–375 °C) and pressure range (5–10 bar) relevant for industrial operation. The microkinetic model used in this study is based on previous work,[43] where we used the Reaction Mechanism Generator (RMG)[53–55] to automatically build the mechanism for a Ni(111) facet. A feasible set of energetic parameters is derived through an ab-initio based theory-constrained optimization that can predict the recorded transient phenomena. We investigate whether Ni(111) can be the active site for methanation and how it responds to transient stimuli. Combined with sensitivity and reaction path analysis, new insights into the possible methanation mechanism under transient high-pressure conditions can be obtained.

Results and Discussion

Experimental results

Forced periodic operation is achieved by alternating the reactor feed between a mixture of H₂/Ar and CO₂/He through switching between two gas lines that result in step changes. Both feeds have identical volumetric flow rates. This “bang-bang” operation was chosen as a test case scenario since it is a straightforward to apply forced periodic operation. The operation mode is characterized by the cycle split ratio γ[13] (Eq. (1)): \[ \gamma = \frac{t_{\text{CO}_2}}{t_{\text{CO}_2} + t_{\text{H}_2}} \] (1) where \( t_{\text{CO}_2} \) is the time during which the reactor is supplied by CO₂ and \( t_{\text{CO}_2} + t_{\text{H}_2} \) is the total cycle time. Values between 0 (pure H₂) and 1 (pure CO₂) can be attained for γ, with 0.2 corresponding to a stoichiometric cycle split ratio. The transient experiments in this study were conducted for a cycle time of 120 s, which is 3.4 τ, where τ is the hydrodynamic residence time of the Berty reactor with 35.5 s for a volumetric flow rate of 395 mL min⁻¹ at 5 bar and 300 °C.[54] Cycle period (\( t_{\text{CO}_2} + t_{\text{H}_2} \)) and response time of the system (τ) are in the same order of magnitude. Therefore, the experiments can be characterized as fully transient.[9]

Figure 1a,b,c show recorded concentration profiles for a temperature of 340 °C and a pressure of 5 bar with different cycle split ratios. Initially, the catalyst is exposed to the H₂/Ar mixture. Upon switching from H₂/Ar to CO₂/He flow, a CH₄, H₂O, and CO formation sets in. The CO₂ signal follows the He signal closely, which indicates that CO₂ has only minor interactions with the catalyst. Interaction with the strong adsorption sites on the support, present on Ni/Al₂O₃ catalysts can lead to a significant delay in the CO₂ response.[44] The SiO₂ support of the Ni/SiO₂ catalyst used in this study does not adsorb CO₂ and the amount of CO₂ adsorbed at elevated temperatures on Ni is also small.[46,55] The CH₄ and CO concentration immediately reach a pattern that remains invariant over the subsequent cycles for the stoichiometric cycle split (γ = 0.2, see Figure 1a). In contrast, the H₂O concentration shows a smaller amplitude for the first step change. The evolving concentration profile after the first step change - the build-up - is more pronounced for the cycle split of 0.5 in Figure 1b. There is no phase shift between the CH₄ and H₂O profiles during the transient operation and both reach their maximum concentration in the H₂ rich part of the cycle. While the CO signal is aligned with the other products in the build-up, a phase shift of 180° is obtained for the following cycles, with the maximum peak height in the H₂ lean part. Five cycles are conducted before the reactor is reverted back to the H₂/Ar mixture. The remaining CO₂ is either converted to CH₄ or leaves the reactor according to the CSTR residence time distribution and the concentrations of the products decline gradually to zero. This part of the experiment is known as the back-transient. While the last peak of CH₄ does not change compared to the limit cycle for the stoichiometric cycle split, a significant overshoot in the concentration is obtained for the ratio of 0.8 in Figure 1c. A similar overshoot is observed for H₂O. The maximum concentration of this overshoot does not exceed the maximum value from the stoichiometric cycle split ratio in Figure 1a. Recorded temperature variations above and below the catalyst basket are limited to ± 1.5 K indicating isothermal behavior, which is supported by CFD simulations.[56] Temperature fluctuations can also be caused by the different thermal conductivity of the gas mixtures during periodic operation.[5,13]

The periodic concentration profiles are challenging to interpret. They are a combination of kinetic effects as well as the physical mixing that determines the residence time distribution of the reactor.[17] A better comparison of the temporal profiles can be obtained in the state space, where the concentration of interest is plotted over the internal standard, in this case, He. Next to a dilution of the gas mixture, the
internal standards track the residence time of the system. If the species follows the internal standard, it is only subject to physical mixing and a straight line from 0 to 1 is obtained. It is possible to present the complete recorded concentration response in a state space, but this is too complex. Therefore, we only focus on the limit cycle. In order to compare different concentrations, it is preferable to normalize the concentration by the maximum peak height $x_{\text{max}}$ and the minimum concentration $x_{\text{min}}$ in the limit cycle according to Eq. (2).

$$x_{j}^{\text{norm}} = \frac{x_{j} - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}}$$  \hspace{1cm} (2)$$

State space plots are clipped to the boundaries of 0 to 1 with this normalization and profiles for the CH₄, CO, and H₂O limit cycle are shown in Figure 1 lower row. This illustration facilitates the identification of the phase shift among the products for a stoichiometric cycle split. In Figure 1d, the CO concentration is high in the CO₂ rich phase whereas the CH₄ concentration is low and vice versa. This changes when the cycle split ratio is altered. For a split of 0.5, the CO concentration increases first with increasing He but reaches a maximum for a He concentration around 0.8 and declines again (see Figure 1e). When switched to H₂, CO formation increases and reaches another maximum at He = 0.5. While all CH₄ and H₂O exhibit only a single maximum in the period, CO shows 2 (see Figure 1b,e). This doubling in the frequency response could point to the presence of two different pathways producing CO, which depend on the gas phase concentration. A similar doubling of the frequency has been observed for some species during dynamic methanation in a plug-flow reactor with a Ni/Al₂O₃ catalyst. The CO state-space profile for the 0.8 split in Figure 1f is again different. The minimum of the peak is reached for the maximum CO₂ concentration and the maximum aligns with the H₂O as well as the CH₄ peak. The maximum peak height is reached in the H₂ rich part, but not at the maximum H₂ concentration.

Microkinetic modeling

The microkinetics for the CO₂ methanation were taken from a previous study conducted by the authors. The reader is referred to ref[43] for a detailed description of the microkinetic mechanism and its development. Briefly, the mechanism was automatically constructed using the open-source Reaction Mechanism Generator (RMG)[53–55] to build a mechanism for the methanation on Ni(111) because it has a high share of the exposed facets and terrace sites are considered to be the active center.[56] Thermochemical properties of the adsorbates were determined from a Pt(111) database[60] and scaled with linear scaling relations to the Ni(111) facet.[61] Activation barriers were estimated based on Brønsted-Evans-Polanyi (BEP) relations.[62] Since DFT-derived parameters, either activation barriers or

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Experimental concentration profiles for a temperature of 340 °C, a pressure of 5 bar and a cycle split ratio of a) 0.2, b) 0.5, and c) 0.8. State space diagrams for the limit cycle of CH₄, CO, and H₂O for the corresponding cycle split ratios a) 0.2, b) 0.5, and c) 0.8. Only the last period is illustrated. The solid line is not a fit but intended to guide the eye. Ar is omitted in the figures for clarity. The arrows indicate the rotation of the limit cycle.
binding energies, are uncertain by 20–30 kJ mol\(^{-1}\).\(^{[50,63,64]}\) It was chosen to propagate the uncertainty in the mechanism generation procedure. 5,000 microkinetic models were generated by perturbing all database parameters within their uncertainty space using a stochastic quasi-random sampling. A correlation was assumed among the key descriptor species for the linear scaling relations,\(^{[65]}\) i.e. H, O, C as well as physisorbed species and for the BEP parameters of each reaction family. Only the activation barriers of the reactions were perturbed, while pre-exponential coefficients were assumed to be constant. Within the given uncertainty space, RMG discovered that 6 gas-phase species, 25 adsorbates and 150 elementary steps are kinetically relevant to describe the CO\(_2\) methanation over Ni(111). All three major CO\(_2\) conversion pathways discussed in the literature were discovered by the automated generation procedure and are part of the mechanism, which are the carbide/redox, carboxyl and formate pathway.\(^{[41,42,44,45]}\) A large part of the mechanism consists of surface abstraction reactions, usually neglected but these can become more important at higher coverages obtained at higher pressures.

Simulations were performed with all 5,000 microkinetic models without any modifications from ref\(^{[43]}\) for all conducted experiments. Typical results are presented in Figure 2a for a temperature of 340 \(^\circ\)C, a pressure of 5 bar, and \(\gamma = 0.5\). The comparison of the predicted and simulated He profile highlights that the Berty reactor behaves as an ideal CSTR, verified also by CFD simulations\(^{[58]}\) and that the reactor model with its parameters is justified. Simulation results from generated models in this global uncertainty assessment (GUA) reveal a broad spread of possible concentration profiles, ranging from no activity for CH\(_4\) formation to very high activity. The experimental results are well within the uncertainty range of

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**Figure 2.** a) Simulation results of the transient concentration profiles with all 5,000 microkinetic models compared in a global uncertainty assessment (GUA) with transient experiments for a temperature of 340 \(^\circ\)C, a pressure of 5 bar, and a cycle split ratio of 0.5. The black line shows the prediction of the best match without coverage effects (w/o \(\theta\)) and the red line with coverage effects (w \(\theta\)). b) Steady-state simulation and experiments for CH\(_4\) and CO at various H\(_2\)/CO\(_2\) ratios, a temperature of 340 \(^\circ\)C, and a pressure of 5 bar. c) Parity plot for CH\(_4\) and CO with and without the inclusion of adsorbate-adsorbate interactions in the microkinetic model for the best match mechanism. Each plot contains around 54,000 data points.
the model, which suggest that Ni(111) could indeed be the active site for the CO₂ methanation. This result was anticipated based on the outcome of the previous study.⁶³ Similar to the transient experiments, a broad spread of results is obtained for the steady-state experiments, which also encloses the experimental results (see Figure 2b). In analogy to our previous work, we can search for the set of parameters in the 5,000 microkinetic models that gives the lowest deviation to all steady-state and transient experiments; the best match mechanism, illustrated as a black line in Figure 2. This best match predicts a too low CH₄ and H₂O concentration in the limit cycle compared to the experiments and a significant overshoot in the back-transient. The simulated CO profile is in reasonable agreement with experiments and even the doubling of the frequency is predicted. Similarly, the microkinetic model is not capable of describing the observed trend for the steady-state results of the CH₄ and H₂O concentration whereas CO is accurately predicted. Parity plots for CH₄ and CO are shown in Figure 2c to assess the accuracy of the microkinetic model for all experiments. First, these parity plots highlight the abundance of data obtained through transient experiments, which makes dynamic kinetic investigations a valuable tool.⁶¹,⁶³,⁶⁶ All data were used to find the best match mechanism, which amounts to roughly 270,000 individual datum. Second, the parity plot demonstrates that the microkinetic model does capture the transient CO profiles accurately, while most of the predictions for CH₄ do not agree with the experiments.

A possible source for the incapability of the microkinetic model to describe CH₄ and CO at the same time is the omission of coverage effects in the microkinetic model. The catalyst surface is usually covered by a combination of O*, CO*, and H* especially at the high-pressure conditions in our experiments. Due to interactions of these species, the coverage affects the stability of the adsorbates and transition states, which ultimately alters the pathways of the microkinetic model.⁶⁴ O* and CO* have strong repulsive interactions,⁶⁷ while H* remains mostly unaffected by other adsorbates. Therefore, we included self-interaction effects on the heat of formation (binding energy) of O* and CO* in all 5,000 mechanisms. As a simplification, the influence of lateral adsorbate interactions with the transition states, the activation barriers, was not considered. Since all reactions are formulated as reversible in Cantera,⁶⁸ the reverse rate is estimated through the equilibrium constant to adhere to thermodynamic consistency. For the reactions where either CO* or O* are a product, the activation barrier of the reverse step is now coverage dependent. In order to constrain the coverage dependence only to the thermochemistry, we rewrote and reparametrized all reactions where either CO* or O* are a product, the activation barrier of the reverse step is now coverage dependent. In order to constrain the coverage dependence only to the thermochemistry, we rewrote and reparametrized all reactions where these two species are a product in the reverse direction to make these species the educts. This limits the effect of coverage-dependent heats of formation on the activation barrier for the reverse reaction in the reversible implementation of the microkinetics. The only exception is the CO* desorption since this barrier depends directly on the binding strength of CO*.

Simulations with the inclusion of coverage effects do not alter the spread of possible solutions. Yet, considerably more microkinetic models exhibit a higher activity (see Figure S5). Through the inclusion of coverage effects, it is no longer possible for either CO* or O* to cover the entire surface, which increases the number of vacant sites and, consequently, the reaction rates. The search for the best match mechanism reveals now a microkinetic model that can qualitatively and semi-quantitatively describe the CH₄ and H₂O profile as well as the CO profile. Table S3 summarizes the microkinetic model and a yaml file of the best match microkinetic model is provided in the SI as well. CO concentrations are slightly underestimated for the second peak in the cycle. The agreement is also significantly improved for the steady-state simulation and the recorded trend can be predicted (see Figure 2b). Still the CH₄ concentration is under predicted in most cases. The comparison with all experiments in the parity plot stresses the significant improvement for CH₄ while the accuracy for CO is conserved.

Figure 3 shows the comparison of the best match microkinetic model for selected experiments, to demonstrate how the performance is for other pressures, temperatures, and cycle split ratios. Results for all remaining experiments can be found in the SI and in the public dataset⁶⁰ along with all scripts. The best match microkinetic model captures the concentration profiles in all displayed cases with great accuracy for CH₄⁴¹,⁶² and CO while H₂O is more challenging to predict (see Figure 3a–c). The discrepancy can also be caused by a larger error bar for the experimental data since H₂O is also challenging to calibrate and measure with an MS. However, the measured water concentration is in some experiments lower than the stoichiometry of the reaction, especially for the cycle split ratio of 0.8 (see Figure 3a). In principal, the H₂O signal is a linear combination of the CO and CH₄ signal due to the reverse water-gas-shift and methanation reaction convoluted by transient processes. The steady-state experiments proof this behavior and demonstrate that this is not a calibration mistake, so there might either be condensation of H₂O in the transfer lines during the transient experiments or a strong adsorption on the stainless-steel tubes facilitated by high CO₂ concentrations. Therefore, we introduce a theoretical H₂O concentration, denoted as H₂O' in Figure 3, based on the measured CH₄ and CO, assuming that only reverse water-gas-shift and CO₂ methanation occur.

This theoretical concentration is in much better agreement with the model predictions. Admittedly, this might not capture the interaction of H₂O with the catalyst in its entirety since this can deviate from CH₄ and CO. Only the CO concentration in Figure 3c is slightly underestimated in the H₂ rich part of the cycle. Experiments and model can also be compared in the state space diagram as illustrated in Figure 4a. Due to the normalization, deviations between model and experiments become even more apparent. The microkinetic model at 340 °C and γ = 0.5 has a small shift for the CO maximum in the H₂ rich part. The decline of the CH₄ signal in the CO₂ half-cycle is faster than measured, but otherwise a good agreement prevails.

Since the microkinetic model can accurately predict the recorded concentration profile, the coverage profiles can now be used to explain the build-up behavior and the back-transients. Only CO* and H* are the adsorbates with a
significant coverage under all investigated conditions. The next most abundant species is O* with coverage values below 2%. CO* reaches a high coverage after the first switch to CO$_2$ and almost remains constant through the entire dynamic experiment. The H* coverage increases slightly during the H$_2$ rich phase of the cycle, which leads to a decrease in the number of vacant sites. This can be better seen in the state-space diagram in Figure 4b. Actually, the H* signal follows the H$_2$ concentration and the CO* and CO profile bear a close resemblance as well. The coverage profiles attain the limit cycle quickly. For the experiment with a cycle split ratio of 0.8 in Figure 3a, a significant build-up and overshoot in the back-transient is observed. However, the coverage profile does not show a build-up of CO* on the surface. From this result, it can be concluded that the overshoot in the back-transient is a gas-phase phenomenon. The increasing H$_2$ concentration in the Berty reactor leads first to a scavenging of the adsorbed CO*. With an increasing number of vacant sites available, more H* can adsorb.

Figure 3. Comparison of experiment and simulation for a) 325°C, 7 bar, γ = 0.8, b) 340°C, 10 bar, γ = 0.5, and c) 375°C, 7 bar, γ = 0.5. d,e,f) Corresponding coverage profiles.

Figure 4. State space diagram of the limit cycle for a cycle split of 0.5 at 340°C and 5 bar. a) Concentration profiles and b) normalized coverage. The arrows indicate the rotation of the limit cycle. Each He mole fraction has two gas-phase concentrations or coverages, depending on the part of the cycle, either H$_2$ rich or CO$_2$ rich.
and react with the CO₂ to CH₄, which fills the Berty reactor. When all the CO₂ is either converted or has left the reactor through physical mixing, the CH₄ concentration shows the typical decline of a CSTR residence time behavior. Additionally, the small amount of catalyst cannot store adsorbed CO* in sufficient quantities to cause the overshoot in its entirety. Although the mechanism can account for the formation of C*, it is not possible to include pathways for the formation of the various carbon pools, which are often predicted for the CO methanation,[80] but not for CO₂.[71]

Figure 5 shows the results from the transient sensitivity analysis to identify the most important reactions and intermediates that control the CH₄ and CO formation. The elementary steps with the highest sensitivity coefficients for CH₄ as well as CO over all experiments are the formation of water and the formation of CH₃* (see Figure 5a). Interestingly, neither the CO₂* dissociation nor the HCO* dissociation, which are often identified in the literature as rate-determining,[41,42] is sensitive towards the methane concentration for the best match microkinetic model. This can be seen in Figure 5a since their sensitivity coefficient is negligibly small for CH₄ as well as CO. However, as shown in our previous study, the rate-determining step changes considerably within the uncertainty space.[43] The HCO* dissociation barrier determines whether Ni(111) is active or not, but when Ni(111) is active, this step is never rate-controlling.[43] CH₃* formation has a positive sensitivity coefficient with respect to CH₄, which means that increasing the rate results in a higher methane formation. For CO this is the opposite. An increase in the water concentration has a positive effect on the CO as well as CH₄ formation. This demonstrates that the formation of CH₃* determines the selectivity of the methanation reaction. The most important surfaces intermediates are H*, H₂O*, and CH₃*, which are displayed in Figure 5b. A destabilization of H* increases CO* formation while decreasing CH₄. H* is in most hydrogenation elementary steps the product and the reverse rate is computed through the equilibrium constant. A decrease in the heat of formation of H* lowers the free energy of the reaction since most of these steps are exothermic, which consequently lowers the equilibrium constant and decreases the reverse rate. The sensitivity coefficient for CH₃* and H₂O* show exactly the same pattern as the corresponding dissociation reactions since these are coupled through the equilibrium constant as well.

Figure 6 shows reaction path analyses conducted at various times during the cycle for a temperature of 340°C, a pressure of 5 bar and a cycle split of 0.5 to gain insights on how the mechanism is affected by the gas-phase composition. Figure 6b represents the reaction path following the carbon element directly after the switch to CO₂. First, CO₂ adsorbs associatively to CO₂*, which dissociates to CO*. Hydrogen-assisted pathways via formate or carboxyl are considerably slower. On the other hand, the CO* forms HCO*, which dissociates to CH* and O*. The methylidyne is then subsequently hydrogenated to CH₄. Desorption of CO has a significantly higher rate than the formation of CH₄ under CO₂ rich conditions. No changes are observed in the reaction path after the switch to H₂ is made (see Figure 6c). In the beginning, the reaction rate for the CO* desorption is still faster than the hydrogenation to CH₄. But with increasing H₂ in the gas phase, the surface coverage of H* increases, which amplifies the methanation pathway. When the H₂ concentration reaches high values in the cycle, for case Figure 6d, there is actually a co-methanation of CO and CO₂. Although the adsorption of CO is quite fast, this step is actually equilibrated and does only contribute to a small extent to the formed CH₄. Mostly, the CO concentration just declines through physical mixing. The CO₂ methanation proceeds on Ni(111) for

**Figure 5.** Sensitivity analysis for the production of CH₄ and CO with respect to the kinetics and thermochemistry of the adsorbates for 340°C, 5 bar and γ = 0.5. Limit cycle of the sensitivity coefficients for the rate constants and b) thermochemistry of the adsorbates. The dotted lines show the sensitivity coefficients for CO and the solid lines for CH₄. Only the most important elementary steps and adsorbates are shown. The arrows indicate the rotation of the limit cycle.
all conditions via the same mechanism with only small differences. This is also the dominant mechanism we observed from this ensemble of 5,000 mechanisms for temperature-scanning methanation experiments with a similar Ni/SiO$_2$ catalyst.\[^{[43]}\] A small portion of the formyl reacts at the investigated time points with CO$^*$ to form COH$^*$. However, the H atom is easily abstracted by O$^*$ to form CO$_2^*$, which creates the loop. The formation of C$^*$ is actually predicted by the mechanism via dissociation of CH$^*$ or through abstraction reactions. This surface carbon is then oxidized to CO$_2^*$ again and does not build up on the Ni(111) facet. The mechanism does not change with pressure, supported by the experimental findings since the normalized limit cycles at various pressure coincide (see Figure S4).

The subset of the full mechanism that contains the relevant chemistry (see Figure 6) is identical to the mechanism discovered in our previous study.\[^{[43]}\] Therefore, further compelling evidence is provided that this mechanism subset governs the activity of Ni(111) in the entire uncertainty range assumed during the mechanism generation procedure. Still, due to the considerable spread of possible solutions within the uncertainty space, we do not dare to conclude definitively whether Ni(111) is the active site of our catalyst. In fact, all of the results from the global uncertainty assessment are reasonable. It needs to be stressed that a crucial step to be more conclusive about the activity and selectivity of specific metal facets for certain reactions is to actually reduce the error bar of the computed DFT energies to enable a more accurate determination of kinetic and thermodynamic parameters.\[^{[72]}\] This requires the usage of more accurate DFT methods, such as hybrid functionals or meta-GGAs,\[^{[52,64]}\] which at the time of publication remain computationally too expensive for a system of this size.

Although the model can describe the experimental results with remarkable accuracy over a broad range of conditions and, to some extent, also the steady-state experiments, we want to make the reader aware of possible errors when using this specific microkinetic model outside of the tested parameter space (275–375 °C and 5–10 bar). Instead, the uncertainty from the DFT-derived parameters should always be propagated. We are aware that there are more phenomena that need to be described for a truly first-principles-based understanding of the methanation on Ni catalyst. Foremost, the shape of the Ni crystal on the support with its multiple facet needs to be considered since all of these exhibit some methanation activity.\[^{[42,48]}\] An assumption we made throughout the entire study is that the catalyst morphology does not change over the course of a transient experiment. The gas-phase atmosphere changes from reductive (H$_2$ rich) to oxidative (CO$_2$ rich), which can lead to partial oxidation of the Ni surface induced by water or traces of O$_2$ in the feed.\[^{[73,74]}\] Great care has been taken to purify the feed as much as possible by using high-quality gas purifiers. Nonetheless, it is possible that changes in the surface state of the Ni can occur, which can affect the concentration profiles. For Ni/Al$_2$O$_3$ or Ni/CeO$_2$ catalysts there is also the complex role of the support in the mechanism that requires attention.\[^{[49,75]}\]

In this study, we systematically perturbed model parameters that correspond to the stationary points on the various potential energy surfaces, and we then selected the mechanism that exhibited the best agreement with all transient and steady-state experiments. In essence, this procedure is a form of theory-constrained optimization. This type of “optimization” is advantageous over more conventional fitting approaches that might treat the binding energies and activation energies as

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**Figure 6.** Detailed reaction path analysis for a transient experiment with $\beta = 0.5$ at 340 °C and 5 bar. It is marked in a) at which time points the reaction path analysis was conducted. b) Reaction path in the CO$_2$ rich part of the cycle. c) Reaction path immediately after the switch to H$_2$ and d) at a high H$_2$ concentration. The thickness of the arrow illustrates the rate of the elementary reaction.
The present study provides an experimental and microkinetic investigation of the transient CO methanation via periodic concentration forcing over a Ni/SiO₂ catalyst in a Berty reactor. A microkinetic model was derived from a set of 5,000 possible mechanisms that were automatically generated considering the global uncertainty space of the DFT-based parameters. When coverage effects for CO* and O* were included in this microkinetic model, it was possible to find a mechanism with a feasible set of parameters in agreement with all transient and steady-state experiments. This model is qualitatively and quantitatively in good agreement with the transient data and can also capture the steady-state experiments, suggesting that Ni(111) could be the active site on our catalyst. Through the microkinetic model, it was possible to gain insights into the mechanism. The methanation reaction proceeds under all conditions via the dissociation of adsorbed CO₂* and H-assisted dissociation of CO*, CH₄*, and H₂O* formation are the steps that control the rate and the selectivity towards CH₄. With this microkinetic model, we explored the complex and non-linear surface dynamics that govern the transient concentration profiles. The microkinetic model can now be used in reactor models to explore the transient behavior in packed bed reactors for Power-to-Gas scenarios.

Methods Section

Catalyst

A 20 wt% Ni/SiO₂ catalyst was produced with a spray-drying method. An aqueous solution of Ni(NO₃)₂ and colloidal SiO₂ with a size of 8 nm were injected into an N₂ carrier gas stream via an atomizer. This carrier gas passed through a tube furnace heated to 400 °C, which leads to one-step calcination and agglomeration of the catalyst building blocks. A filter was placed downstream of the furnace to collect the nanoparticles that were then heat-treated at 400 °C under air for 3 h to complete calcination. The nanoparticles were pelletized using a disk pelletizer. An aqueous solution of the colloidal SiO₂ was used as a binder and the catalyst pellets were calcined under the same conditions as before. A sophisticated physical and chemical characterization of the particles is provided in ref. The Ni surface area was determined via H₂ adsorption. A value of 222 μmol g⁻¹ was obtained, which corresponds to a metal surface area of 17.4 m² g⁻¹ and a dispersion of 13%.

Experimental setup

The transient methanation experiments were conducted with a Berty reactor from Integrated Lab Solutions ILS (Berlin, Germany). A P&ID of the process unit is provided in the SI and described in detail in ref. Gases were of quality 5.0, except CO₂ (4.5), and were further purified by gas traps (VICI AG) to decrease contaminants (H₂O, O₂, S) below 1 ppb. Gas mixtures were prepared with mass flow controllers (EL-Flow Select, Bronkhorst). Two gas lines are installed in the unit to enable step changes between different feeds. Both lines are connected to the similar back-pressure regulators (U3 L, Equilibar) equipped with a PTFE glass laminate membrane at the same dome pressure, which minimizes pressure differences when switching between them. The gas mixture is preheated before entering the Berty reactor, whose design is described in detail in ref. A turbine sits above a catalyst basket with an inner diameter of 10 mm. A stream of Ar with a volumetric flow rate of 95 mL min⁻¹ is constantly flushed over the cooled turbine shaft to prevent condensation and exposure of the magnet.
to H₂. Temperature readings are provided by type K thermocouples above and below the catalyst. The exhaust line of the reactor and back-pressure regulators were kept at 200 °C. Concentrations of the exhaust are recorded by a mass spectrometer (GAM 200, Inprocess Instruments) with a two-staged gas inlet operated at 200 °C. The external standard Ne (20 mℓₐ min⁻¹) was added to the exhaust directly in front of the MS using a special mixing chamber (Bronkhorst). This allows for tracking pressure changes as well as changes in the flow rate due to the methanation reaction. Thus, a measurement of the volumetric flow rate at the resolution of the MS is provided. The yttriated iridium filament was operated at a low cathode voltage of 50 V to prevent strong fragmentation of the molecules, which facilitates their accurate quantification; signals were amplified with a secondary electron multiplier at 1350 V.

The MS was calibrated with certified gas mixtures using Ar as internal standard and compared to a reference mixture, ensuring sufficient accuracy for all components. Calibration of water was done in a methanation experiment where a high selectivity to CH₄ was obtained. Mass-to-charge ratios are measured in an upwind direction with a dwell time of 0.1 s.

### Transient methanation experiments

80 mg of the catalyst were placed in the basket between layers of quartz wool and stainless steel meshes of 40 μm. A rotation speed of 8,800 min⁻¹ was used in all experiments and it was demonstrated that this results in homogeneous gas-phase concentrations and also isothermal conditions. Reduction was performed with a H₂/Ar mixture at a temperature of 450 °C for 12 h approached with 5 K min⁻¹ at 5 bar. The reactor is alternated between a mixture of 30% H₂ in Ar and 30% CO₂ in He. Both volumetric flow rates were set to 300 mℓₐ min⁻¹. He and Ar are used as internal standard to simplify the evaluation of the reaction rates,¹⁴,¹³¹ to dilute the gas mixture to reduce hot spots and to track the residence time of the system.¹⁴,¹³¹ Cycle split ratios of 0.2, 0.5, 0.8 for a cycle time of 120 s were used in the experiments at temperatures from 275–375 °C and pressures of 5, 7, and 10 bar. Five cycles were performed, where the start and end mixture is H₂/Ar. A more detailed description is provided in the SI. In addition, steady-state experiments were conducted, where the catalyst was kept at a fixed temperature for 30 min for various H₂/CO₂ ratios. All parameters for the methanation experiments are summarized in Table S1.

### Microkinetic modeling

Simulations of the transient methanation experiments were conducted with the open-source Cantera⁶ program. The Berty reactor was modeled as an ideal CSTR assuming isothermal behavior. No mass transport limitations between catalyst and gas phase were assumed. Additionally, it was assumed that the catalyst efficiency is unity, meaning that diffusion limitations are absent, which is justified due to the small catalyst particle size of approximately 80–150 μm. All reaction steps were treated as fully reversible, ensuring thermodynamic consistency. Forward rate constants were specified via an Arrhenius equation and the reverse rate constant is estimated through the equilibrium constant, which is computed based on the thermochemistry of the adsorbates.⁶⁰,⁶¹ Coverage-dependent heats of formation for the self-interaction of CO* and O* were taken from Grabow et al.⁶² approximated by a second-order polynomial (see SI for details). Simulations were performed with all 5,000 generated microkinetics from ref.⁶³ and compared to the experiments using the weighted mean-absolute percentage error (WMAPE) (Eq. (3)):

\[
WMAPE = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{M_i - P_i}{\sum_{j=1}^{N} M_j} \right|
\]

where M is the measured value, P is the prediction of the model, and N is the number of points. A sensitivity analysis for the kinetics \( \Sigma_{rate} \) (Eq. (4)) and thermochemistry \( \Sigma_{thermo} \) (Eq. (5)) was conducted with respect to the mole fraction of CH₄ and CO in analogy to the degree of rate control analysis.⁶⁴,⁶⁵

\[
\Sigma_{thermo} = \frac{1}{x_i} \left( \frac{\partial x_i}{\partial \gamma} \right) \left( \frac{\partial \gamma}{\partial T} \right)
\]

\[
\Sigma_{rate} = k_i \left( \frac{\partial k_i}{\partial T} \right)
\]

### Acknowledgements

BK thanks the Alexander von Humboldt Foundation for financial support through a Feodor Lynen postdoctoral scholarship. BK and CFG gratefully acknowledge support by the U.S. department of Energy, Office of Science, Basic Energy Sciences, under Award #000023253, as part of the Computational Chemical Sciences Program. We acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project number: 290019031. Open Access funding enabled and organized by Projekt DEAL.

### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.6506655, reference number 69.

**Keywords:** Methanation · Dynamic operation · Microkinetic modeling · Kinetics · Heterogeneous catalysis

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