

# 1D Simulation of Direct Carbon Dioxide Conversion to Methane over NiO-SiO<sub>2</sub> Catalyst Using Detailed Surface Chemistry

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## 1 Introduction

Until 2050, a renewable energies capacity increase about 8,5 GW per year is required. A broad mix of different energy sources combined with the usage of the existing energy infrastructure enables flexible, economic and robust transformation paths and energy supply. Even if huge efforts are made to push alternative mobility concepts such as electric cars (BEV) and fuel cell powered cars and even if BEVs are gaining ground, the importance and use of liquid fuels is expected to stay high during the 2030s [31]. Within this context biomethane and synthetic natural gas [26, 28, 29] may play a key role as they are suitable and for power generation and for mobile applications and can replace natural gas without any infrastructure changes [16].

Within this paper, we aim to understand the direct production of synthetic natural gas from CO<sub>2</sub> and H<sub>2</sub> in a Sabatier process based on a thermodynamically consistent elementary reaction mechanism. For that purpose, a series of NiO-SiO<sub>2</sub> catalysts with varying Ni content have been experimentally investigated. The rate and selectivity of CO<sub>2</sub> methanation were explored at reactor temperatures around 420 °C and volume flows from 50 - 500 ml min<sup>-1</sup>. Efforts have been made in the 1D model to describe the material properties as well as the physical and flow properties of the reactors as accurately as possible in order to avoid incorporating physical effects in the mechanism.

The typical temperature range for the Sabatier process is 250-400°C, ensuring a high conversion rate and a minimum of side reactions, and thus a high selectivity towards methane [12, 19]. Common methanation catalysts are based on noble metals, nickel and its oxide, or the combination of them on different substrates such as CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and MgO [18]. The noble metals Rh, Ru and Pd have been reported to be highly catalytically active for the Sabatier process [2, 4, 5, 9, 13, 17, 20, 21, 33]. However, in view of profitability NiO<sub>2</sub> is often the catalyst of choice as NiO<sub>2</sub> catalysts combine the advantage of moderate process temperature and pressure combined with a high methane yield and selectivity as well as affordable cost [11]. In thermodynamic equilibrium at 300°C, a methane yield of 95% with a selectivity close to 100% can be achieved at stoichiometric feed gas composition of 80% hydrogen and

20% carbon dioxide [15]. Higher temperatures favour the endothermic reverse water-gas shift reaction resulting in carbon monoxide formation.

To maximize the activity, selectivity and stability of chemical reactors in general and the Sabatier reactor in particular, the converters are subject to continuous improvement. While experimental optimization entails high expenses in terms of cost and time, virtual optimization is a promising alternative. However, despite its enormous technical and economic significance the understanding of heterogeneous catalysis lags behind the paramount economic success in various chemical industry processes [6]. Likewise, the exact reaction mechanism of methanation in Nickel-based catalysts is still subject to debate and kinetic models applicable at the industrial scale are rare [14, 15, 27, 30], even if the material has been widely studied because of its low cost and wide availability [32]. Thus, simulation models for heterogeneous catalysts are often based on empiric observations. Given the reactor specific character of these models, they need to be trained prior to their use for different reactors with changed geometry or composition.

The key to the virtual design of new catalysts with optimized performance lies in the detailed understanding of the physical and chemical properties of the catalyst as well as the underlying chemical reactions at a molecular level. Within this paper, we present a method to develop and validate a detailed kinetic mechanism based on detailed knowledge of the given catalyst that is valid over a broad range of boundary conditions. The method rests on the validation of a detailed reaction mechanism based on the mechanism published by [8] using tailor-made experiments. The detailed micro-kinetic analysis combined with experimental tests is a powerful method that allows to derive qualitative and quantitative information about catalytic reactions at the molecular level.

## 2 Materials and Methods

### 2.1 Experimental

In this work, fixed bed reactor measurements with different amounts of nickel based catalytic material were performed at varying boundary conditions. A conversion and yield of above 90% and a selectivity of nearly 100% were measured in the laboratory setup. Optimal parameters for the process were studied by variation of reactants volume flow and amount of catalyst inside the reactor.

In the framework of the experiments a nickel oxide catalyst on a silica substrate NiO-SiO<sub>2</sub> was used. The flow rates of CO<sub>2</sub> and H<sub>2</sub> were increased step by step (in a ratio of 1:4), usually at constant furnace temperature. Depending on the amount of catalytic material and activity of the catalyst, the reactor temperature increased. The experiments were carried out with a 5 cm<sup>3</sup> reactor. A comprehensive set of transient data with varying volume flow has been recorded to develop a kinetic model that captures the intrinsic kinetics of the methanation of carbon dioxide under different conditions. The experimental setup is shown in figure 1.

The investigated reactors have the same geometry as described in table 2.1. The compared reactor setups only differ in terms of the content of catalytic material. Even if carefully done, it cannot be guaranteed that the catalytic material is uniformly distributed within the reactor. Furthermore, the higher the amount of applied NiO on the SiO<sub>2</sub> support, the higher the probability of NiO clusters that have a smaller surface than highly dispersed catalytic material. That is why the value of catalytic activity (surface area per catalyst length) is not behaving directly proportional to the amount of NiO. Indeed, the given values are the result of a sensitivity analysis.

Table 1: The geometric data and catalyst parameters used to carry out the simulations.

Set-up	0.1 g	0.2 g	0.5 g
Open Volume [%]		48	
Length [m]		$1.0 \times 10^{-2}$	
Diameter [m]		$4.0 \times 10^{-3}$	
Washcoat thickness [m]		$4.0 \times 10^{-3}$	
Washcoat porosity [%]		70	
Surface area per catalyst length [m]	$2.2 \times 10^{-3}$	$5.81 \times 10^{-3}$	$1.89 \times 10^{-2}$

## 2.2 Modelling

The 1D model, LOGEcat [1] is utilized to carry out the simulations. This model is a part of the LOGEsoft software suite for chemical reaction calculations. The model is based on the single-channel 1D catalyst model and is applicable to the simulation of all standard after-treatment catalytic processes [3, 7, 10] as well as chemical reactor modelling e.g. steam reforming of methane over nickel [22–25]. The model has been successfully applied and tested in past studies [3, 7, 25]. For more details related to the model and the model equations, we refer the reader to our previous papers [3, 7, 22].

The investigated mechanism initially contains 54 reactions based on the mechanism published by [8]. Reaction kinetics are taken into account using the Arrhenius approach with prefactor, temperature exponent and activation barrier. The forward rate constant,  $k_{f,r}$ , for the reactions  $r$  are generally presumed to have the following Arrhenius temperature dependence (for gas-phase as well as surface species),

$$k_{f,r} = A_r T^{\beta_r} \exp\left(\frac{-E_r}{R_c T}\right), \quad (1)$$

here,  $A_r$  is the pre-exponential factor,  $\beta_r$  is the temperature exponent and  $E_r$  is the activation energy. The gas temperature is represented by  $T$  and  $R_c$  is the gas constant in units consistent with activation energy. Equation (1) is used to calculate the irreversible reaction rate constants, thus the rate coefficients ( $A_r$ ,  $\beta_r$  and  $E_r$ ) are specified for all reactions in the chemistry input file.

Mechanism training of the catalyst has been performed using a comprehensive sensitivity analysis using LOGEcat [1]. Here, rate determining steps can be evaluated and rate parameters can be trained in order to meet the experimental results at different catalyst compositions and reactor conditions. Due to the experimental conditions, thermodynamic and kinetic phases alternate such that reaction kinetics can be investigated and trained. Indeed, for each investigated catalyst and for each investigated volume flow, the experiments are performed such that thermodynamic equilibrium is always achieved before change of inlet conditions and before passing over to the next condition.

## 3 Results

Figure 2 compares the experimental and virtual results of the conversion of carbon-dioxide and hydrogen to methane and water at 700 K inlet temperature for increasing volume flow in three different reactors. The inlet flow always consists of 80 % hydrogen and 20 % carbon-dioxide. Each step represents a volume flow increase of 100 ml starting from 100 ml.

Several conclusions can be drawn from that figure. At the first glance, it is obvious and expected that increasing amounts of catalytic material entail higher methane and water yields. However, this effect is

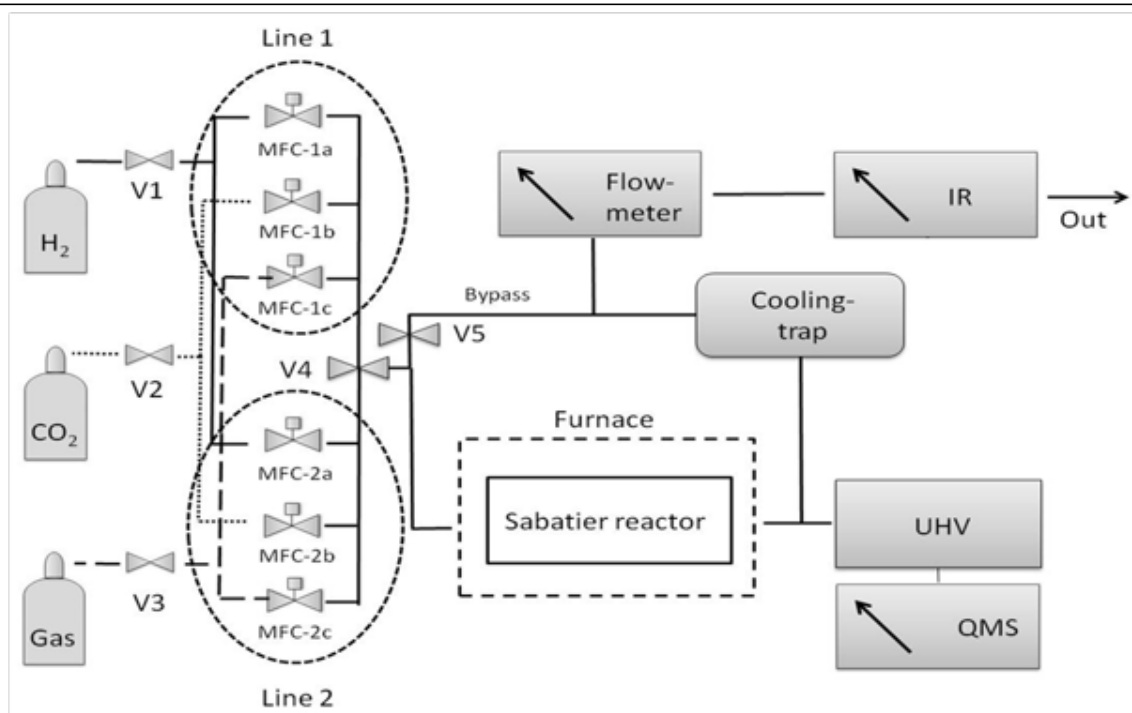


Figure 1: Experimental setup of Sabatier process.

not linear. That is to say that the increase in methane mole fraction from the reactor with 0.1 g NiO to the reactor with 0.2 g NiO is much more pronounced than when one compares the methane mole fraction of the 0.2 g NiO reactor with that of the 0.5 g NiO reactor. This effect can be explained by agglomeration effects of the catalytic material as well as a certain saturation effect for a given reactor size.

Figure 2 further illustrates that the experimental methane yield decreases with increasing educt mass-flow. This behaviour is also expected as the residence time of the inlet gas decreases with increasing massflow. Furthermore, the surface of the catalyst can only adsorb and convert a certain amount of molecules. The higher the gas inlet flow the faster the surface is saturated such that no educt gases can be adsorbed anymore.

When it comes to compare the slopes of the measured methane mole fractions of the three different reactors it is apparent that the higher the catalyst amount the flatter becomes the decreasing slope of methane and water mole fraction. This behaviour is also expected as the higher the amount catalytically active material in the reactor, the more molecules can be adsorbed. Higher amounts of catalytic material dampen the negative effect of increasing massflow on the methane yield.

When comparing the experimental results with the virtual results in figure 2 it can be concluded that the 1D simulation model is able to predict the methane and water concentrations downstream the catalyst to a very high extend especially for the two less active catalysts. The model is not able to predict the slope of the most active catalyst with high accuracy. However, all the experimentally observed effects are also reproduced by the simulation results: the methane yield increases with higher amount of NiO, this effect shows a saturation behaviour. Moreover, the methane yield decreases with increasing volume flow and the decrease is dampened with higher amount of NiO in the reactor.

We can try to explain the deviations between experimental and simulated results for the 0.5 g NiO reactor at the highest volume flows. It is possible that the 1D monolithic model is not able to capture the physics of the fixed bed reactor, this may result in deviations that are due to differences in residence time or in the thermal behaviour of the catalyst. Another reason could be that boundary conditions in the third

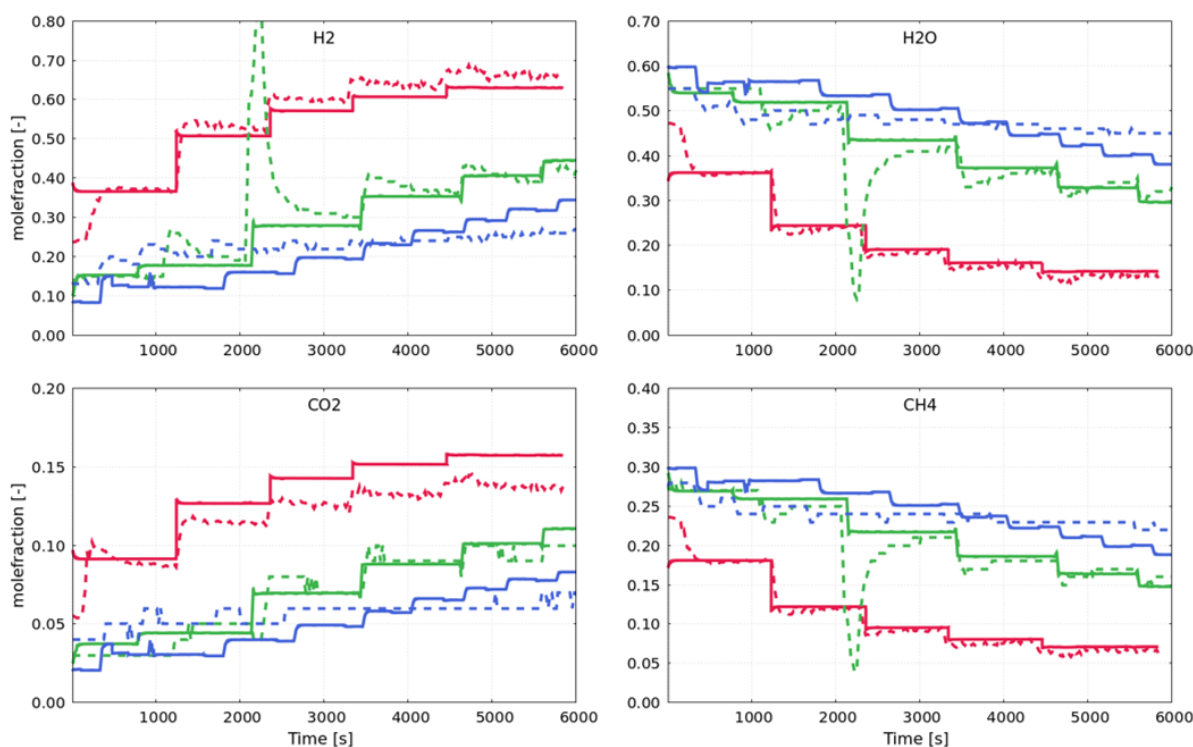


Figure 2: Comparison of experimental (solid line) and simulated (dashed line) species mole fractions for three different reactor loadings (0.1 g (red), 0.2 g (green), and 0.5 g (blue) of active material, respectively.

reactor are outside of the valid range of the mechanism. In order to shed more light on the capacities of mechanism, the production of CO has to be considered. Unfortunately, CO mole fraction has not been measured during the experimental campaign. Thus, we will only look at the simulated CO results. Figure 3 shows the simulated CO mole fraction together with the simulated reactor temperatures of the three investigated reactors. It is obvious that the level of CO production considerably differs between the reactors with 0.1 and 0.2 g NiO on one side and the reactor with 0.5 g NiO on the other side.

Temperature ranges for the Sabatier process between 250-400°C ensure a high conversion rate and a minimum of side reactions [12, 19]. Higher temperatures favour the endothermic reverse water-gas shift reaction resulting in carbon monoxide formation. The temperature of the most active reactor rises up to more than 600°C, thus the high simulated amount of CO is not surprisingly. Here, further investigations are required to understand if the temperature rise is correct and to understand in more detail the kinetics of CO formation via the endothermic reverse water-gas shift reaction.

#### 4 Conclusion and Outlook

In this paper, a one-dimensional model has been used to validate the chemical kinetics for direct conversion of hydrogen and carbon-dioxide over a nickel/alumina catalyst at 700 K such that the model can be used for virtual catalyst development within the shown boundary conditions. It is worth noting that the cost effective reduced order (1D) model is capable to capture the physics and chemistry showing the predictive capability of the model. The results are compared with experimental data. The simulation results of the validated kinetic model were found to be consistent with the experimental data at almost all shown operating conditions and catalyst composition. In a next step, the model is further investigated with regard to the CO production via the reverse water gas shift reaction. It is also planned to apply

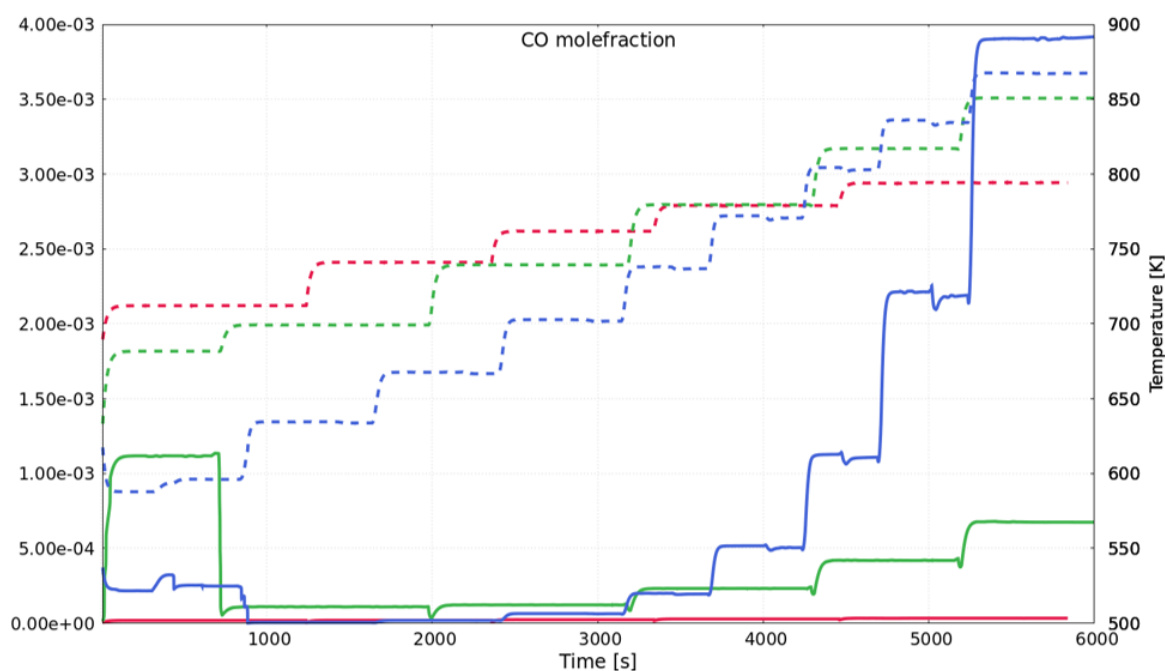


Figure 3: Comparison of simulated CO mole fraction (solid line) and simulated temperature downstream the catalyst (dashed line) for three different reactor loadings (0.1 g (red), 0.2 g (green), and 0.5 g (blue) of active material, respectively).

the model to other Ni-containing catalysts with different catalytic load to further validate the kinetic mechanism.

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