

An Experimental and Computational Study on the Impact of Key Parameters on Methane Steam Reforming over a Ni/Al₂O₃ Catalyst

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1 Abstracts

In this study, a 1D catalyst model is validated using experiments on steam reforming of methane utilizing a Ni/Al₂O₃ catalyst. The experiments were conducted with a comprehensive parameter study varying the mass flow rates and pressures, and the results were thoroughly evaluated in the study. The experiments were designed with two important features in mind: First, the catalyst was loaded with different catalytic surfaces along its length, and second, reaction kinetics were considered by measuring an axial temperature profile. Such measurements allow one to take a deeper look into reaction kinetics and not just work in the region of near thermodynamic equilibrium. The model presented in this study showed a good agreement with the experimental measurements, providing valuable insight into this complex reaction system.

2 Introduction

Steam reforming is a widely used industrial process for producing hydrogen gas from hydrocarbons such as natural gas. The process involves reacting the hydrocarbons with steam in the presence of a catalyst to produce hydrogen and carbon monoxide. Steam reforming is a key process in the production of hydrogen for various applications, including the production of ammonia for fertilizers, refining petroleum, and fueling fuel cells for clean energy. [1,2]

The modeling of steam reforming is of great importance in view of the debate on hydrogen as the energy carrier of the future. It provides an extremely valuable approach that allows researchers to gain a deeper understanding of complex scientific phenomena. Modeling involves creating abstract representations of systems and processes, which enables analysis and prediction of their behavior. The model developed and applied in this study shows good agreement with the experimental measurements. A 1D catalyst model is validated with a detailed kinetic reaction mechanism using experiments on steam reforming of methane. The utilized catalyst is a Ni/Al₂O₃ catalyst. The experiments were conducted with a comprehensive parameter study varying the mass flow rates and pressures, and the results were thoroughly evaluated in the study. The experiments were designed with two important features in mind: First, the catalyst was loaded with different catalytic surfaces along its length, and second, reaction kinetics were considered by measuring an axial temperature profile. Such measurements allow one to take a deeper look into reaction kinetics and not just work in the region of near thermodynamic equilibrium which shows the significant part of this study.

3 Model Description

The basic frame for the used model in this work is the single-channel 1D catalyst model approach introduced by [3] where the catalyst is modeled as a single pipe with a user given number of cells with length Δx (see Figure 1). Each cell is treated like a perfectly stirred reactor (PSR). For all PSRs the conservation equations for mass, heat and flow are solved. The model is extended with the multi-channel approach presented in [4]. The multi-channel approach models multiple catalyst channels with the consideration of heat conduction in between the channels to represent the transient heat transfer more physically. For more details on species and energy transport, the reader is referred to the cited works. In Figure 1 the basic concept of the model is shown. Within this study only steady-state single-channel calculations were performed. The physical parameters of the experimental fixed-bed reactor were chosen according to the fixed-bed reactor dimensions and the open volume of the fixed-bed reactor was assumed to be the same as the open volume of the virtual monolithic reactor in LOGEcat [5]. The reaction mechanism applied for the simulations in this work includes methane and water decomposition on the nickel (Ni) and is based on [6]. The mechanism contains 13 species and 42 reactions with the Langmuir-Hinshelwood approach.

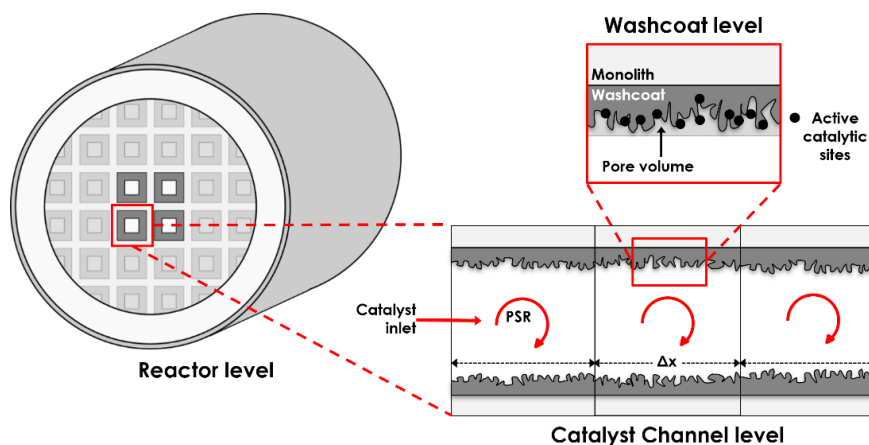


Figure 1: Model concept and discretization of a channel (with the cell length Δx). [7]

4 Experimental setup

Within the scope of this work, experiments were carried out with different catalyst dilutions. The dilution was carried out here with Al_2O_3 spheres, with an identical diameter of 2 mm to the catalyst material. A reactor length of 30 cm was selected, and the catalyst bed was divided into three 10 cm long segments with different loadings. Dilution to 10% (1/10) catalyst material was performed at the gas inlet, dilution to 20% (1/5) in the middle, and no dilution (100%) was performed in the last segment. The high dilution at the inlet serves to limit the amount of CH_4 that can react, due to the small catalytic surface area, and thereby reduce the temperature drop. A segment without dilution at the outlet is intended to ensure that CH_4 , which has not yet been able to react, is in contact with the catalytically active surface, and the reaction can proceed completely here. The measurements were carried out at a GHSV of 3000 to 9000 1/h, corresponding to inlet volumes of 0.33 to 1 L/min of methane. Figure 2 shows the experimental setup.

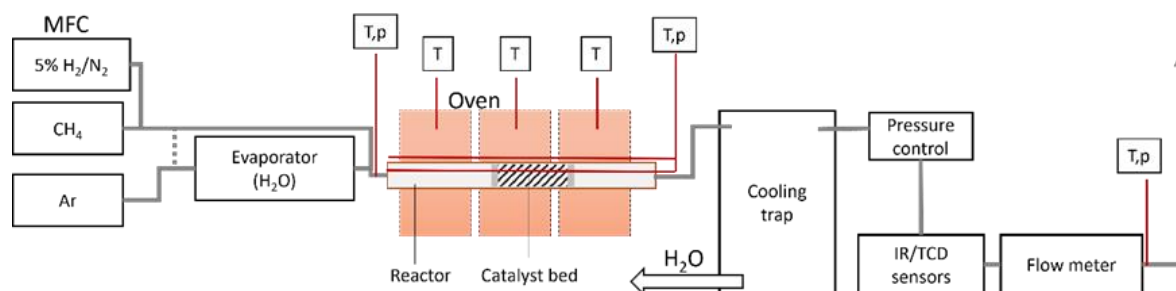


Figure 2: Experimental setup, with MFCs to control the individual gas flow rates, evaporator, temperature (T) and pressure (p) measurement, cooling trap to remove residual water, pressure control for system pressure adjustment, gas analytics via infrared and thermal conductivity detector, and flow meter.

5 Simulation Setup

The geometrical parameters for the simulation setup were taken directly from the experiments. The thermodynamic data is based on Nasa polynomials from [8]. The heat flux from the external oven was taken into account by radial heat exchange between the catalyst and its surrounding. Each simulation was carried out until steady state was reached, resulting in a simulation time of 170 s. For the simulation of the 30 cm long experimental catalyst a representative circular single-channel is used and split into 25 equidistant cells. This discretization was tested in a preliminary calculation. The steady inlet gas species concentration and gas conditions can be seen in Table 1. In Table 2 the physical input parameters for the 1D model reactor can be found.

Table 1: Steady inlet gas parameters.

Parameter	Unit	Fixed-bed reactor model
Inlet gas composition	Mole fraction [-]	CH ₄ : 0.331; H ₂ O: 0.669
Inlet gas temperature	K	1025
Inlet gas pressure	10 ⁺⁰⁵ Pa	1.013, 2.000, 3.000, 4.500
Inlet massflow	10 ⁻⁰⁵ kg/s	1.28

The simulations were carried out on an AMD Opteron Processor 2389@2900MHz system on 8 CPUs simultaneously with a CPU time of around 40 min.

Table 2: Physical input parameters for 1D model reactor.

Parameter	Unit	Fixed-bed reactor model
Catalyst outer geometry	-	Circular
Channel geometry	-	Quadratic
Number of cell	-	25
Channel density	10^{+05} 1/m^2	4.64
Catalyst length	m	$3.0 \cdot 10^{-01}$
Catalyst radius	10^{-03} m	4.85
Hydraulic diameter	m	$1.05 \cdot 10^{-03}$
Surface area per catalyst length (changed after every 10 cm)	m^2/m	$1.00 \cdot 10^{-02}$, $2.00 \cdot 10^{-02}$, $1.00 \cdot 10^{-01}$

6 Results

Figure 3 shows a variation of GHSV for a pressure of 1 bar. It can be seen that with increasing GHSV and thus increasing velocity and mass flow, the endothermic reaction along the reactor is enhanced and the minimum temperature is more pronounced. This trend is also reproduced by the model. It can be seen that for GHSV 3000 1/h the minimum temperature is in zone 1, where a dilution of the catalyst of one 1/10 prevails. For GHSV 6000 1/h, the minimum temperature is already shifted to zone 2 and to a dilution of 1/5 catalyst. For GHSV of three 9000 1/h, the minimum temperature is in zone 3 at the maximum catalyst loading in the reactor. This is because increasing the GHSV decreases the residence time in each reactor zone, and thus the potential for the gas to react with the active surface and perform the full endothermic reaction. Thus, here in the case of e.g. GHSV 9000 1/h in zone 1 and 2 little contact of the gas with the surface is carried out due to the dilution and only in the last zone where only catalyst prevails the whole reaction can take place almost abruptly. It can be seen that the model still has difficulties in capturing the exact endothermic temperatures measured in the experiment. Furthermore, the model shows a too strong shift of the endothermic minimum temperature, this may be due to problems in the transfer of the exact velocities and residence times in the reactor due to the transfer from fixed bed reactor to monolith reactor. This behavior is still being investigated and adjusted. The emissions out of the catalyst show a good agreement with the simulations and can be seen in Figure 3 on the left side of the Figure. It is visible that by increasing discrepancy between experiments and simulations in the temperature profile also the emissions start to shift. In the course of the experiments, variations of the pressure between 1 bar - 4.5 bar were carried out, which can be seen in the Figure 4 and Figure 5. It is visible that by increasing pressure the results for GHSV 3000 1/h are improving while for GHSV 6000 1/h – 9000 1/h there is still more room for improving.

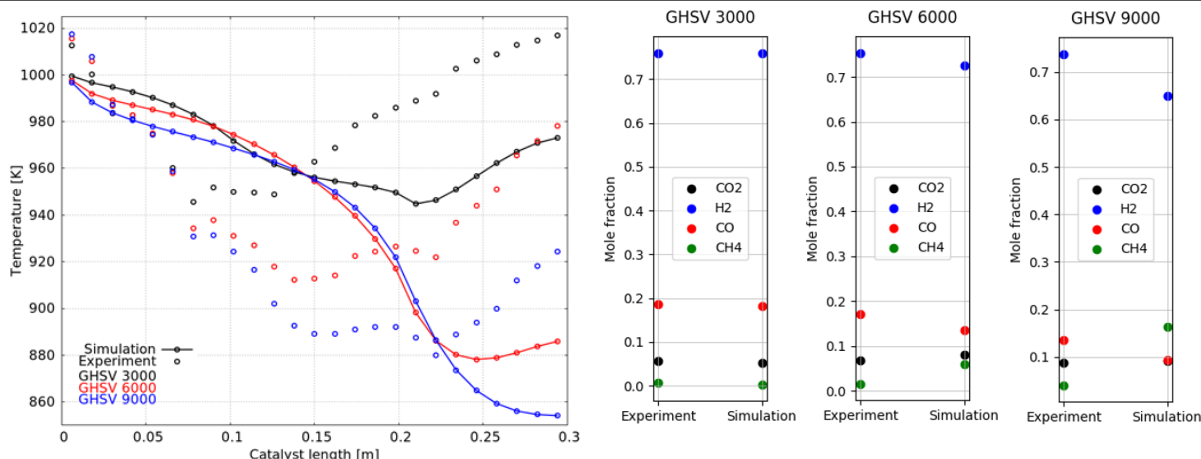


Figure 3: Temperature profile over the catalyst length for varied GHSV experiments in the fixed-bed reactor at 1bar (left) and emissions out of catalyst (right) at 1 bar.

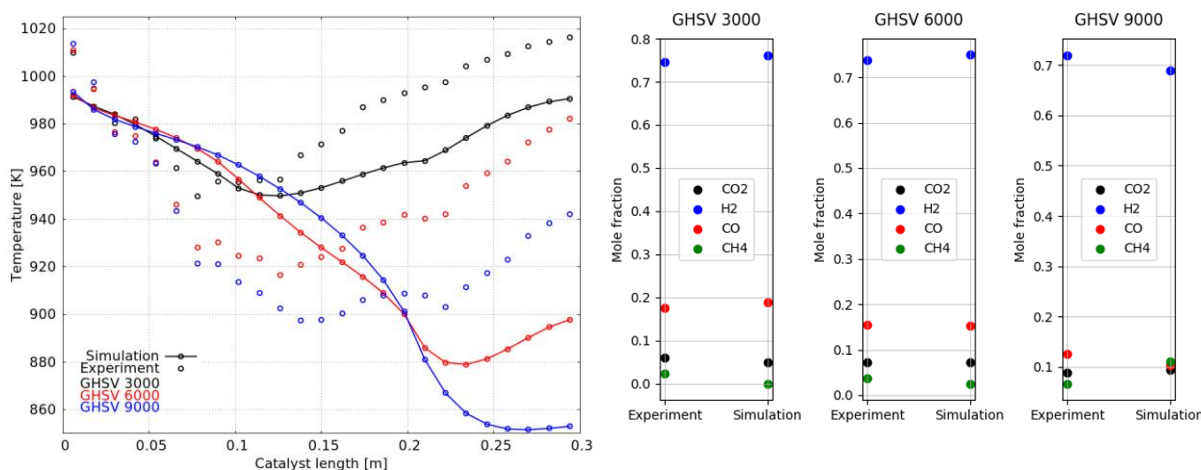


Figure 4: Temperature profile over the catalyst length for varied GHSV experiments in the fixed-bed reactor at 2 bar.

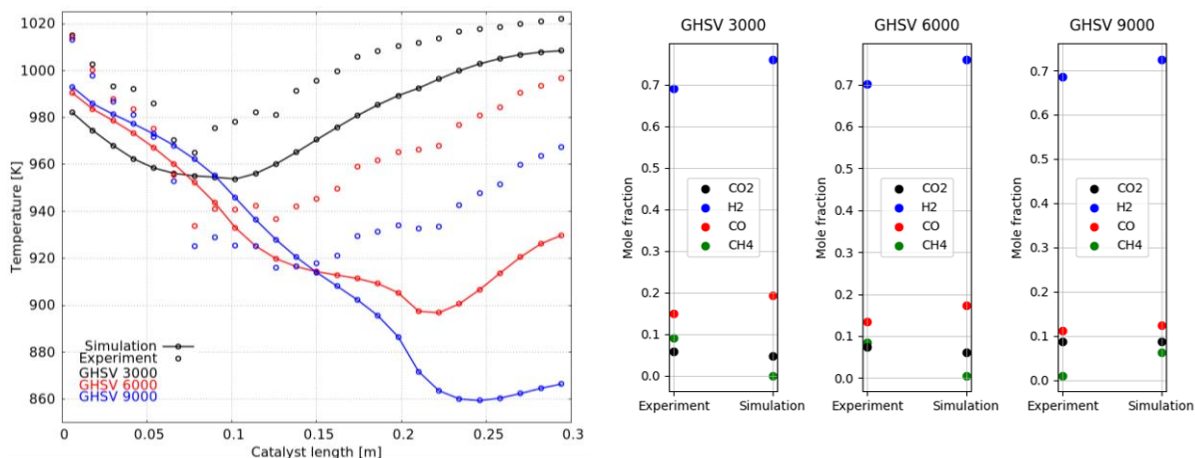


Figure 5: Temperature profile over the catalyst length for varied GHSV experiments in the fixed-bed reactor at 1bar (left) and emissions out of catalyst (right) at 4.5 bar.

Conclusion

In this work, experiments on steam reforming in a fixed-bed catalyst reactor were performed. A particular focus was on a variation of the reforming parameters. The different dilution of the catalyst along the reactor offers interesting insights into the reaction progress. By varying the GHSV as well as the dilutions, a good insight into the process could be obtained. Following the experiments, computational fast 1D simulations were carried out which showed good agreement with the experiments. As part of this work, variations of pressure were also demonstrated. The particular measurements of the temperature profile along the catalyst length give unique insights into the kinetics of the reaction and ensure that the focus is not only on the emissions and thus on the thermodynamic equilibrium.

Acknowledgments

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