

# Catalytic CO<sub>2</sub> Methanation: Providing Optimal Test Conditions for Kinetic Investigations

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DOI: 10.1002/cite.202200201

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In the context of using renewable energies and recycling climate-changing gases, methanation of CO<sub>2</sub> provides one possibility. However, volatile availability of renewable energies for hydrogen production and fluctuating CO<sub>2</sub> streams from different sources lead to enhanced demand in investigating the influence of dynamic process operation on the catalyst performance, including detailed kinetic characterization. Reliable kinetic measurements require isothermal temperature control and absence of macrokinetic diffusion limitations. Both were investigated in this work while the determination of steady-state kinetic parameters is part of ongoing studies. Furthermore, a detailed analysis with respect to the long-term-stability of the nickel-based catalyst was performed.

**Keywords:** CO<sub>2</sub> methanation, Kinetics, Long-term stability, Ni catalyst, Power-to-Gas

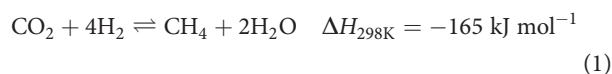
*Received:* November 14, 2022; *revised:* January 06, 2023; *accepted:* February 09, 2023

## 1 Introduction

Global consumption of fossil resources related to anthropogenic activities led to increased CO<sub>2</sub> emissions in the atmosphere [1]. Today, the use of renewable energies and recycling of climate-changing gases are of increasing importance. In this context, methanation of CO<sub>2</sub> with electrolytically produced hydrogen from renewables enables chemical energy storage in a cycle (Power-to-Gas) [2] and contributes to the reduction of CO<sub>2</sub> emissions [2–4]. The production of synthetic natural gas (SNG) is of increased interest since it can easily be stored and transported in the already existing gas infrastructure, while being reused for energy generation on demand. Coupling this technology to small, decentralized CO<sub>2</sub> sources such as biogas plants raises new research challenges regarding fluctuating process conditions and feed gas impurities [5]. This leads to specific requirements with respect to the applied catalyst and the overall process design. Future research activities at the University of Applied Sciences in Düsseldorf will contribute to this topic by investigating the catalytic CO<sub>2</sub> methanation under dynamic operation conditions using a nickel-based catalyst. For this purpose, a kinetic characterization over a wide range of conditions from differential conversions to thermodynamic equilibrium is required. Moreover, for precise kinetic measurements, various boundary conditions must be met. Thus, explicit measurements were carried out in order to ensure isothermal conditions and absence of macrokinetic diffusion limitations.

The catalytic hydrogenation of CO<sub>2</sub> to methane (Eq. (1)) was first reported by Sabatier and Senderens in 1902 [6–8]. CO<sub>2</sub> methanation, the so-called Sabatier reaction, is revers-


ible, exothermic, and thermodynamically favorable [9, 10]. According to Le Chatelier's principle, the reaction is favored at low temperatures and increased pressure due to volume contracting. However, significant kinetic limitations exist and therefore, a catalyst is required in order to achieve acceptable rates and selectivities [10, 11]. Depending on catalyst and reaction conditions, catalytic methanation is operated at temperatures above 250 °C and pressures between 1–30 bar, predominantly in fixed bed reactors [12, 13].



Research on methanation of CO<sub>2</sub> focuses on different catalyst systems. Up to now, noble metal catalysts provide the highest performance, with ruthenium considered the most active metal for CO<sub>2</sub> methanation [11, 12]. However, catalyst systems based on non-noble metals, e.g., nickel as a well-known representative of this group, are significantly more cost-effective. In most cases, the catalytically active metals are deposited on a support and combined with various promoters to achieve higher activity and long-term stability. Al<sub>2</sub>O<sub>3</sub> is the most widely studied support material

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as it provides a large specific surface area leading to high and homogeneous metal dispersion. [13]

A detailed review on Nickel-based catalyst systems, the mechanism of the methanation reaction as well as typical effects for catalyst deactivation applied under steady-state conditions was recently published [14].

## 2 Experimental

### 2.1 Experimental Setup

Investigations were conducted in a lab-scale flow setup that allows testing of heterogeneous catalysts in a tubular reactor under various reaction conditions. The process flow chart of the facility is shown in Fig. 1. The setup provides gas supply and mixing, a reactor section as well as online gas analysis. Gases are dosed by mass flow controllers (MFC) and water can be added by a saturator before entering the reactor section. The reactor section consists of a horizontal quartz glass tubular reactor in a high-temperature oven. Ni/Al<sub>2</sub>O<sub>3</sub> diluted with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as inert material was used as benchmark catalyst. The catalyst bed was fixed with quartz wool in the reactor. The oven temperature, the temperature on the outside of the reactor as well as the temperature of the catalyst bed can be measured by individual thermocouples. To prevent condensing, all tubing is heated. The product gas finally reaches the online gas analyzer behind a gas cooler, which is equipped with three infrared and one thermal conductivity detector.

### 2.2 Catalyst Synthesis

Nickel catalysts with a Ni-loading of 20 wt % were prepared by wet impregnation method adopted from Le et al. [15]. The support material  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (>99.9 % Merck,

$S_{\text{BET}} = 140 \text{ m}^2 \text{ g}^{-1}$ ) was fractionated prior to impregnation to achieve a particle size of 0.5–0.8 mm. 10 g of the support material were added to the aqueous solution obtained by dissolving a defined amount of nickel nitrate hexahydrate (>99 % Acros Organics) in 30 mL deionized water. The resulting mixture was heated at 95 °C and the excess water was slowly removed at reduced pressure using a rotary evaporator. The fraction was dried in an oven at 105 °C for 16 h followed by calcination in flowing air at 450 °C for 2 h. For reduction, the catalyst was heated up in the reactor to 450 °C by 10 °C min<sup>-1</sup> in a 10 vol % H<sub>2</sub> in N<sub>2</sub> flow and kept for 45 min.

### 2.3 Isothermal Temperature Control

In order to meet the first boundary condition of isothermal temperature control, various temperature tests under kinetically relevant conditions were performed. By altering the horizontal position of the thermocouple in the fixed bed, a temperature profile of the oven was determined. For this purpose, two inert beds of different lengths were installed in the reactor and the temperature was measured at different positions in various distances. After the bed temperature was constant in each case, the data point was averaged over one minute. The reactor was flowed through with 200 mL<sub>N</sub> min<sup>-1</sup> N<sub>2</sub>.

Since the reaction is strongly exothermic, the oven temperature does not reflect the actual temperature in the catalyst bed. Therefore, the bed temperature was recorded over time while setting different oven temperatures in order to determine a correlation of the oven and catalyst bed temperature. Here, steady-state operating points were established for 60 min at 250 °C, 270 °C, 290 °C, and 310 °C, respectively, under the same reaction conditions as in the long-term stability test.

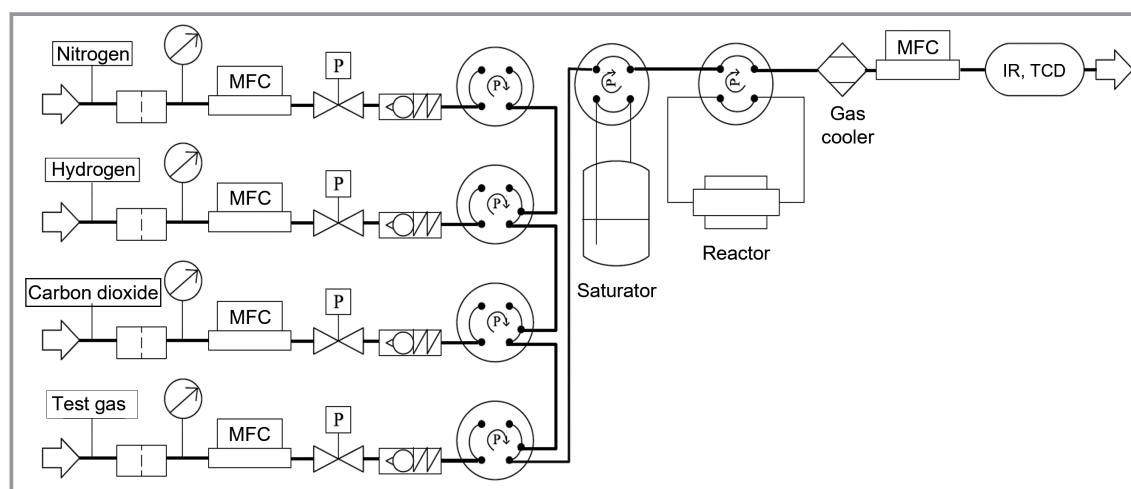


Figure 1. Process flow chart of the laboratory flow setup.

## 2.4 Macrokinetic Diffusion Limitations

The presence or absence of the influence of external diffusion on the reaction rate can be investigated flow rate while keeping the overall contact time constant. The contact time is defined as the ratio of catalyst mass and feed volume flow. If external diffusion has a limiting influence, CO<sub>2</sub> conversion would increase with an increasing flow rate. [16] The influence of external diffusion was investigated by simultaneously varying the catalyst mass between 18 mg, 24 mg, and 30 mg (fraction of 500–800 μm) keeping the overall contact time constant at 6 s kg<sub>cat</sub>m<sup>-3</sup>.

The presence or absence of the influence of internal diffusion on the reaction rate can also be investigated experimentally. For this purpose, CO<sub>2</sub> conversion can be determined by varying the particle size of the catalyst under otherwise identical conditions. If pore diffusion has a limiting influence, CO<sub>2</sub> conversion would increase as the catalyst particles become smaller [16]. Therefore, the catalyst particle size was varied applying fractions of 160–355 μm, 355–500 μm, 500–710 μm, and 500–800 μm, respectively. The catalyst mass was constant at 24 mg providing a constant contact time of 6 s kg<sub>cat</sub>m<sup>-3</sup>.

For both investigations, steady-state operating points were established at 250 °C, 270 °C, 290 °C, and 310 °C, respectively. The catalyst mass was diluted with a dilution ratio of catalyst mass to inert material of 1:4 for these investigations. To ensure steady state conditions and reproducibility, the catalyst was first exposed to the particular conditions for 60 min and the data points were averaged over one minute.

## 2.5 Long term stability

In order to ensure constant activity during parameter variation for the subsequent investigation of the CO<sub>2</sub> methanation microkinetic, a long-term test was performed. As the activity of catalysts can decrease significantly with increasing reaction time, parameter variation should only be carried out after a possible initial deactivation phase. Potential deactivation mechanisms for methanation catalysts, known mainly from CO methanation, are poisoning and thermal degradation [17]. Therefore, a detailed analysis with respect to the long-term-stability of the catalyst was performed. In this investigation, 24 mg of the Ni-catalyst diluted with 96 mg γ-Al<sub>2</sub>O<sub>3</sub> were examined under steady-state reaction conditions at a temperature of 290 °C for 700 h. The contact time was kept constant at 6 s kg<sub>cat</sub>m<sup>-3</sup> applying a gas composition of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 4:1:3.

## 3 Results and Discussion

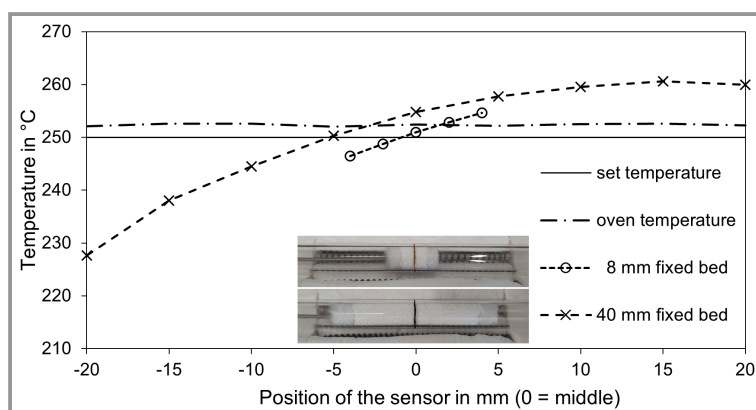
### 3.1 Isothermal Temperature Control

To obtain the temperature profile of the oven, the position of the temperature sensor was varied horizontal along the reactor. In Fig. 2, the set temperature and measured oven temperature as well as the fixed bed temperature over the position of the thermocouples are shown. Here, the oven position 0 mm corresponds to the center of the fixed bed as well as the center of the oven, and the reactor is flowed through from the left.

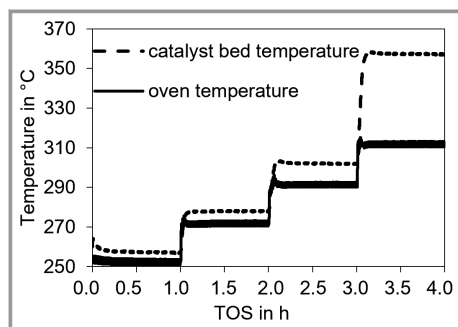
On average, the measured oven temperature was approximately 2 °C above the set temperature. Depending on the length of the bed, temperature gradients between the set temperature and the bed temperature have occurred. In the center of the bed, the difference between oven and fixed bed temperature was the lowest. These results indicate a limited isothermal zone in the middle of the oven. Thus, the bed should be as small as possible and centered.

Since the reaction is strongly exothermic, the oven temperature does not reflect the temperature in the catalyst bed. To determine temperature-related effects of the exothermic reaction, the temperature of the oven as well as the bed temperature were recorded while the reaction was taking place. Fig. 3 shows the bed and oven temperature for different set values (250 °C, 270 °C, 290 °C, 310 °C) over time on stream (TOS).

Initially, reaction heat was generated, and the bed temperature increased. In principle, the difference between oven and bed temperature became more significant as the set temperature increases. However, isothermal measurement conditions can be guaranteed by an indirect temperature control based on this experimentally derived correlation of the oven and catalyst bed temperature. Considering the strong exothermic temperature increase for a set temperature of 310 °C, future kinetic measurements will be carried out at temperatures below 300 °C.



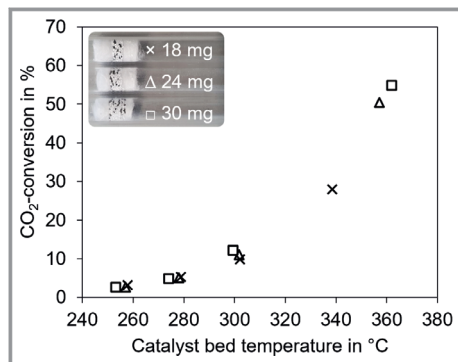
**Figure 2.** Horizontal temperature profile of two inert fixed beds of different length in the reactor.



**Figure 3.** Oven temperature and catalyst bed temperature over time on stream.

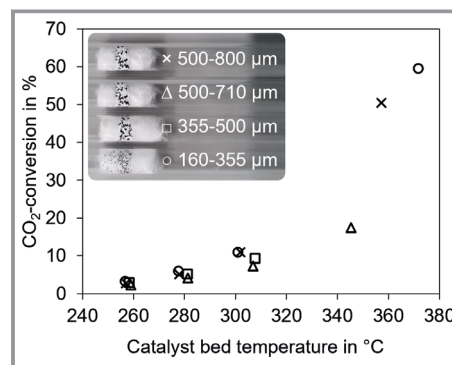
### 3.2 Macrokinetic Diffusion Limitations

The influence of external diffusion was investigated by simultaneously varying the catalyst mass and flow rate keeping the overall contact time constant. Fig. 4 shows  $\text{CO}_2$  conversion over the catalyst bed temperature. The overall  $\text{CO}_2$  conversion remained almost constant when the catalyst mass and flow rate were varied. In addition, experiments with the highest flow rate have not shown the highest  $\text{CO}_2$  conversion and experiments with the lowest flow rate have not shown the lowest  $\text{CO}_2$  conversion. These results indicate that external diffusion limitations can be excluded within the considered conditions.



**Figure 4.**  $\text{CO}_2$  conversion over the catalyst bed temperature for the varied catalyst mass at a constant contact time of  $6 \text{ s kg}_{\text{cat}}\text{m}^{-3}$ .

In order to investigate internal diffusion limitations, the catalyst particle size was varied applying fractions of 160–355  $\mu\text{m}$ , 355–500  $\mu\text{m}$ , 500–710  $\mu\text{m}$ , and 500–800  $\mu\text{m}$ , respectively. Fig. 5 shows the  $\text{CO}_2$  conversion over the catalyst bed temperature for the internal diffusion investigations. The overall  $\text{CO}_2$  conversion remained almost constant when the catalyst particle size was varied. In addition, experiments with the largest particles have not shown the lowest  $\text{CO}_2$  conversion and experiments with the smallest particles have not shown the highest  $\text{CO}_2$  conversion. This led to the conclusion that internal diffusion limitations can also be excluded within the considered conditions.

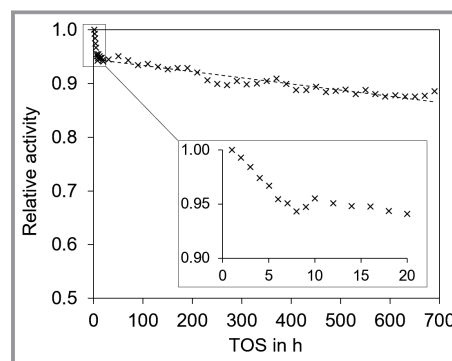


**Figure 5.**  $\text{CO}_2$  conversion over the catalyst bed temperature for the varied catalyst particle sizes.

As shown in Figs. 4 and 5,  $\text{CO}_2$  conversion reached values above 10 % for a set temperature of 310 °C. Since these data points were outside the kinetic range, they were not considered for the investigation of macrokinetic diffusion limitations. To determine the reaction mechanism, it is necessary to ensure that only microkinetic effects (adsorption, surface reaction and desorption) are rate-determining. The results clearly indicate that within the chosen boundary conditions kinetic parameters can be determined with the presented set-up in the future.

### 3.3 Long-Term Stability

In order to ensure constant performance during subsequent parameter variation as part of the ongoing kinetic investigations, a detailed analysis with respect to the long-term stability of the catalyst was performed. For this purpose, 24 mg of the Ni-catalyst diluted with 96 mg  $\gamma\text{-Al}_2\text{O}_3$  were investigated under steady-state reaction conditions at 290 °C for 700 h. The relative activity over the time on stream achieved is shown in Fig. 6.



**Figure 6.** Relative activity over 700 h time on stream.

Here, a relative activity of 100 % corresponds to 10.2 %  $\text{CO}_2$  conversion. A significant drop in activity was detected within the first 8 h TOS, as shown in Fig. 6. The activity of



the Ni-catalyst has finally decreased to 88% after 700 h TOS. The deactivation behavior of the catalysts is approximated in Fig. 6 applying a linear model between 10–700 h TOS.

Previous insights with respect to deactivation were usually generated under steady-state conditions. However, the need for dynamic operation due to fluctuating gas streams is of increasing importance, both technically and academically. In this context, it is important to reveal the influence of dynamic operation on the long-term performance of the catalyst and to clearly distinct these additional effects from steady deactivation. As a conclusion, future Investigations will be carried out after an aging time of 10 h TOS.

## 4 Conclusion

Reliable and reproducible kinetic measurements in heterogeneous catalysis require isothermal temperature control as well as absence of macrokinetic diffusion limitations. Both were successfully achieved in this work. Furthermore, a detailed analysis with respect to the long-term-stability of the catalyst was performed. Due to the observed strong initial deactivation future investigations will include an aging time of 10 h TOS prior to kinetic measurements. Additionally, these measurements will be carried out at temperatures below 300 °C. Thus, steady-state kinetic parameters will be determined and used for modeling the Ni-catalyzed CO<sub>2</sub> methanation. Based on these investigations, the influence of dynamic process conditions on the performance of the catalyst will be subject of future studies.

## Acknowledgment

Open access funding enabled and organized by Projekt DEAL.

## Symbols used

$\Delta H_{298K}$  [kJ mol<sup>-1</sup>] standard enthalpy of reaction

## Abbreviations

SNG synthetic natural gas  
TOS time on stream

## References

- [1] S. N. Riduan, Y. Zhang, *Dalton Trans.* **2010**, 39 (14), 3347–3357. DOI: <https://doi.org/10.1039/b920163g>
- [2] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, *Renewable Energy* **2016**, 85, 1371–1390. DOI: <https://doi.org/10.1016/j.renene.2015.07.066>
- [3] K. Hashimoto, M. Yamasaki, K. Fujimura, T. Matsui, K. Izumiya, M. Komori, A. El-Moneim, E. Akiyama, H. Habazaki, N. Kumagai, A. Kawashima, K. Asami, *Mater. Sci. Eng., A* **1999**, 267 (2), 200–206. DOI: [https://doi.org/10.1016/S0921-5093\(99\)00092-1](https://doi.org/10.1016/S0921-5093(99)00092-1)
- [4] J. Lefebvre, M. Götz, S. Bajohr, R. Reimert, T. Kolb, *Fuel Process. Technol.* **2015**, 132, 83–90. DOI: <https://doi.org/10.1016/j.fuproc.2014.10.040>
- [5] S. Schiebahn, T. Grube, M. Robinius, L. Zhao, A. Otto, B. Kumar, M. Weber, D. Stolten, in *Transition to Renewable Energy Systems* (Eds: D. Stolten, V. Scherer), Wiley-VCH, Weinheim **2013**.
- [6] P. Sabatier, J.-B. Senderens, *C. R. Hebd. Seances Acad. Sci.* **1902**, 134, 689–691.
- [7] P. Sabatier, J.-B. Senderens, *C. R. Hebd. Seances Acad. Sci.* **1902**, 134, 514–516.
- [8] G. A. Mills, F. W. Steffgen, *Catal. Rev.* **1974**, 8 (1), 159–210. DOI: <https://doi.org/10.1080/01614947408071860>
- [9] E. Baraj, S. Vagaský, T. Hlinčík, K. Ciahotný, V. Tekáč, *Chem. Pap.* **2016**, 70 (4), 395–403. DOI: <https://doi.org/10.1515/chempap-2015-0216>
- [10] K. P. Brooks, J. Hu, H. Zhu, R. J. Kee, *Chem. Eng. Sci.* **2007**, 62 (4), 1161–1170. DOI: <https://doi.org/10.1016/j.ces.2006.11.020>
- [11] W. Wei, G. Jinlong, *Front. Chem. Sci. Eng.* **2011**, 5 (1), 2–10. DOI: <https://doi.org/10.1007/s11705-010-0528-3>
- [12] P. Frontera, A. Macario, M. Ferraro, P. Antonucci, *Catalysts* **2017**, 7 (12), 59. DOI: <https://doi.org/10.3390/catal7020059>
- [13] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, *Fuel* **2016**, 166, 276–296. DOI: <https://doi.org/10.1016/j.fuel.2015.10.111>
- [14] P. Strucks, L. Failing, S. Kaluza, *Chem. Ing. Tech.* **2021**, 93 (10), 1526–1536. DOI: <https://doi.org/10.1002/cite.202100049>
- [15] T. an Le, J. K. Kang, E. D. Park, *Top. Catal.* **2018**, 61 (15–17), 1537–1544. DOI: <https://doi.org/10.1007/s11244-018-0965-7>
- [16] W. Reschetilowski, *Einführung in die heterogene Katalyse*, Lehrbuch, Springer, Berlin **2015**.
- [17] C. H. Bartholomew, *Appl. Catal., A* **2001**, 212 (1–2), 17–60. DOI: [https://doi.org/10.1016/S0926-860X\(00\)00843-7](https://doi.org/10.1016/S0926-860X(00)00843-7)