




Methanation of CO₂ from flue gas: experimental study on the impact of pollutants

Gabriel E. de Araujo² · Jéssica H. de Castro² · Wesley F. Monteiro¹ ·
Jeane de Lima^{1,2} · Rosane A. Ligabue^{1,2} · Rogerio V. Lourega³ 

Received: 18 August 2021 / Accepted: 14 October 2021 / Published online: 30 October 2021
© Akadémiai Kiadó, Budapest, Hungary 2021

Abstract

The current work determines the maximum concentrations of pollutants that interfere significantly in the process, mainly in the catalyst. With this, the study tested the impact of oxygen, sulfur dioxide and nitrogen monoxide on NiO/SiO₂ commercial catalyst more used in this process. Besides this, from reactions with and without contaminants, the catalyst was characterized through TGA, FESEM and TEM in order to evaluate the impact of each element on its morphology. Experiments with the presence of the oxygen showed that the O₂ consumes the hydrogen and produces more water, reducing the CO₂ conversion and CH₄ formation. Sulfur showed a significant impact at the reducing of its activity catalyst in concentrations above 5 ppm. Nitrogen monoxide, which is a major component of NO_x showed to be little harmful to the catalyst, changing the reaction stability at the CO₂ conversion. Both NO and SO₂ changed the catalyst morphology and ripped apart the nickel particles from the support, decreasing the catalyst activity over time.

Keywords Methanation · Flue gas · Carbon dioxide · Pollutants · Catalyst poisoning

Introduction

The high human-caused CO₂ emissions increase the concentration of this gas in the atmosphere, turning the natural process of the greenhouse effect into a very current and harmful environmental problem [1–3]. Nowadays, about 85% of the world's energy sources are yet substantially based on fossil fuels [4] and the burning process

✉ Rogerio V. Lourega
louregarv@gmail.com

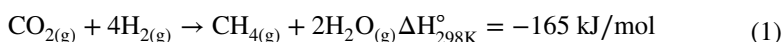
¹ Graduate Program in Materials Engineering and Technology, Pontifical Catholic University of Rio Grande do Sul - PUCRS, Porto Alegre, Brazil

² School of Technology, Pontifical Catholic University of Rio Grande do Sul - PUCRS, Porto Alegre, Brazil

³ INDPROS, Barão de Ubá Street, 48 / 601, Porto Alegre, RS, Brazil

of fossil fuels results in a mixture of gases containing CO_2 , NO_x , SO_x , H_2 , N_2 and numerous other compounds harmful to the atmosphere, called flue gas. Currently, flue gas is one of the major sources of CO_2 to the atmosphere, leading to the need to develop new technologies that can capture and storage (or transform) this gas to mitigate its environmental effects [5, 6]. Processes aiming the chemical conversion of CO_2 are the most common options to reduce the emission of this pollutant and still obtain a product with higher market value. Among several chemical process options, methanation is a promising alternative for using CO_2 from the flue gas, since it produces pure methane that can be stored, burned for thermal or electrical purpose and even used as fuel for transport [7].

Methanation research dates for over 100 years, first being observed by the French chemist Paul Sabatier in 1902 working with CO-methanation [8]. As environmental issue became more and more important, the same principals of monoxide reaction were applied to study methanation (or hydrogenation) of carbon dioxide, which consists on its conversion into methane and water, as shown in Eq. 1 [9].



In order to achieve acceptable values of conversion and selectivity towards methane, carbon dioxide methanation requires the use of a catalyst due to the kinetic limitations. A promisor catalyst to an industrial application needs been easy to synthesize and recyclable. Although metals such as Ru, Rh, Pd, among others, exhibit excellent low-temperature activity toward CO_2 methanation, they cannot be applicable for the industry because of the high price [10]. Other metals such as Co and Fe are relatively suitable for low-temperature CO_2 methanation, they usually performed low CH_4 selectivity [11]. In this context, nickel-based catalysts are a greater option because it is a cheapest active compound, and beside these, adsorbs hydrogen, leading to higher reaction yields and is highly selective for methane formation [12].

Besides the catalyst choice, operating temperature and pressure, reactor design, bed shape and gas feed mixture (e.g. presence of pollutants) directly influence the selectivity and conversion of CO_2 to CH_4 [8]. Due to the reaction kinetics, the operating temperature is usually kept between 250 and 550 °C, varying for isothermal and adiabatic process, while higher reaction pressures can enhance the CO_2 conversion, reason why most reactors operate from 5 to 30 bar [9, 13–15]. Regarding the reactor and bed design there is a wide variety of options, from which the most applied in industrial scale is the adiabatic fixed bed reactor. At last, the ideal gas feed mixture would be a clean mixture of carbon dioxide and hydrogen, on a ratio of 1:4, since any other component can easily change the reaction efficiency (e.g. oxygen). However, in industrial scale, achieving a mixture of CO_2 and H_2 without any other component is extremely hard and costly, especially when the reactants sources originally contain poisoning elements for the catalyst, such as sulfur or chlorine [8].

In order to better understand the possibility of using flue gas as CO_2 source for methanation, recent studies have been analyzing the effect of contaminants in the feed gas to the catalyst activity. The average composition of flue gas from a power plant based on coal is 65.2% (v/v) of N_2 , 18.8% H_2O , 11.6% CO_2 , 4% O_2 , 0.35% SO_x and 0.05% NO_x [7]. Some studies showed that the presence of sulfur in the feed gas

causes considerable loss of the catalyst activity, being limited to less than 10 ppbv in order to guarantee an acceptable catalyst lifetime [16–18]. Concerning NO_x effects on the catalyst activity, different studies tested NO_2 influence on the methanation reaction and found no negative effect [19, 20]. At the same time, oxygen presence on the feed gas can be considered pollutant, since the oxygen consumes the hydrogen that was supposed to form methane and produces water, which decreases the equilibrium conversion of the reaction [7].

Due to the high number of parameters that can affect the reaction performance, thinking on CO_2 direct methanation becomes a challenge. The absence of more complete works studying the effect of different pollutants concentration over the methanation reaction and its effect to the catalyst activity results in an opportunity for new research. Therefore, this work aims to perform methanation reactions investigating the influence of most important pollutants found in flue gas streams. Besides that, the study has the objective of better understanding, through different characterization techniques, the impact of these elements to the catalyst morphology.

Materials and methods

Reaction system

Hydrogenation reactions of carbon dioxide to methane were performed using a gas phase reaction system developed by the authors based in previous works presented in the literature [16, 21–23]. Fig. S1 presents a schematic of the methanation reaction apparatus. This system can be divided into three different sections. The first one is the gas handling part, responsible for controlling and adjusting the reactant gases operational conditions. The six different gases used for the reactions are: carbon dioxide (Air Products 5.0), hydrogen (Air Products 5.0), nitrogen (Air Products 4.0), oxygen (Air Products 4.0), nitrogen oxide mixture (Linde 375 ppm NO/N_2) and sulfur dioxide mixture (Linde 125 ppm SO_2/N_2). The four main gases have their inlet pressure controlled by independent pressure regulators (Rotarex) and their flow adjusted as necessary for each experiment using independent mass flow controllers from Alborg and Omega. The two mixtures (NO and SO_2) are used alternatively in each experiment, since they share the same pressure and mass flow controllers. After the volumetric ratio of each gas is controlled by their mass flow controllers, the gases are sent to a mixer which has the aim of delivering a homogeneous mixture to the reactor. The mixture composition is confirmed using a sampling apparatus which allows to sample the gas with a syringe and analyze it in a gas chromatograph. At the end of this gas handling section, the mixture inlet pressure is indicated by a pressure transducer (Novus 520 Series) located just before the reactor inlet.

The reaction apparatus section is composed of a stainless steel (Swagelok 316/316L steel) tubular reactor set inside a horizontal tubular furnace (Sanchis). The reactor has an internal diameter of 1/2 pol and a total length of 30 cm, with a connection in the middle of its length. This connection is used to easy the process of organizing the catalyst bed inside the reactor, besides being responsible for separating the reactor into two zones. The first one is the reactant heating zone, where glass

spheres are used to increase the heat exchange inside the reactor and heat up the reactants to the desired reaction temperature, before getting in contact with the catalyst. After these spheres, a quartz wool is used to hold the catalyst and separate it from heating section of gas. In this part of the reactor, a thermocouple (Novus type J) is used to control the temperature at the beginning of the catalyst bed, reducing the chances of hot spots formation.

Since the aim of this study was to understand the effect of the different compounds found in flue gas streams, a commercial catalyst (Sigma-Aldrich) was used for these methanation reactions. Nickel oxide supported on silica catalyst (60 wt% NiO) was selected with an average grain size of 0.15 to 0.25 mm. In order to avoid hot spot formation, this catalyst was distributed in a bed of silica gel (Vetec) with the same grain size of the catalyst using a catalyst/silica weight ratio of 1/15. After the catalyst, another quartz wool is set to keep the bed at a fixed position inside the reactor.

The last part of the system is the product handling section, where the gaseous product pressure is controlled in order to keep the reaction at a constant pressure. After that, a sampling system similar from the reactants one is used to sample the products in order to analyze its composition.

Experimental parameters

According to the literature, the gas hourly space velocity (GHSV), one of the most important parameters on a gas phase catalytic reaction, can range largely from one study to another. In studies similar to the one developed by the authors, it was found that the GSHV for bench scale experiments is usually kept between 500 and 25,000 mL h⁻¹ g⁻¹ [24–28]. Since the objective of the study was to analyze the impact of different pollutant concentration over the catalyst structure, not aiming for kinetic mechanism determination, a GHSV of 15,000 mL h⁻¹ g⁻¹ was chosen for all reactions, making sure that the reactions were able to achieve high conversion when using pure reactants.

Thus, a total bed weight of 7.0 g was used for all the experiments, from which 6.5625 g was silica gel and 0.4375 g were catalyst (NiO/SiO₂, corresponding to 60% NiO), resulting in 3.51 mmols of NiO. Before starting the methanation reaction, the catalyst bed was reduced under a hydrogen atmosphere using 20 mL min⁻¹ of pure hydrogen at a constant temperature of 400 °C. Methanation reactions were done according to the experiment planning presented on Table 1. In all scenarios the reaction temperature was kept constant at 350 °C, because according to Muller et al. [7], this ideal temperature, demonstrates that the NiO/SiO₂ catalyst, under atmospheric conditions, provides a greater yield and greater selectivity in the formation of methanation.

The difference between one experiment and the other was the volumetric ratio of each gas in the gaseous stream, even though always applying the same GHSV (total volumetric flow constant at 100 mL min⁻¹). While H₂/CO₂/N₂ volumetric ratio was always kept at 4/1/5, the oxygen and pollutants flows were manipulated

Table 1 Operational parameters used in methanation reactions performed with 0.4375 g of catalyst at 350 °C and with a H₂/CO₂/N₂ volumetric ratio of 4/1/5

| Entry | Time (min) | Description* | Volumetric flow (mL min ⁻¹) | | | | | |
|-------|------------|-------------------------|-----------------------------------------|-----------------|----------------|----------------|-----------------|--------|
| | | | N ₂ | CO ₂ | H ₂ | O ₂ | SO ₂ | NO |
| 1A | 1530 | Stability test | 50.0 | 10.0 | 40.0 | – | – | – |
| 2A | 120 | 2% Oxygen | 49.4 | 9.9 | 39.5 | 1.2 | – | – |
| 2B | 120 | 4% Oxygen | 48.8 | 9.8 | 39.0 | 2.4 | – | – |
| 2C | 120 | 6% Oxygen | 48.2 | 9.6 | 38.5 | 3.7 | – | – |
| 2D | 120 | 8% Oxygen | 47.5 | 9.5 | 38.0 | 5.0 | – | – |
| 3A | 120 | 5 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0003 | – |
| 3B | 120 | 10 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0006 | – |
| 3C | 120 | 20 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0012 | – |
| 3D | 120 | 50 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0030 | – |
| 3E | 120 | 100 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0060 | – |
| 3F | 300 | 5 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0003 | – |
| 3G | 300 | 20 ppm SO ₂ | 50.0 | 10.0 | 40.0 | – | 0.0012 | – |
| 4A | 120 | 25 ppm NO | 50.0 | 10.0 | 40.0 | – | – | 0.0015 |
| 4B | 120 | 50 ppm NO | 50.0 | 10.0 | 40.0 | – | – | 0.003 |
| 4C | 120 | 100 ppm NO | 50.0 | 10.0 | 40.0 | – | – | 0.006 |
| 4D | 120 | 200 ppm NO | 50.0 | 10.0 | 40.0 | – | – | 0.012 |
| 4E | 720 | 100 ppm NO | 50.0 | 10.0 | 40.0 | – | – | 0.006 |

*Concentration in dry basis related to flue gas stream, in this case represented only by N₂ and CO₂

to simulate usual concentration of these elements in flue gas streams. The experimental parameters are summarized in Table 1.

According to published methodologies [7, 29] and in order to better understand the effect of SO₂ presence on a flue gas direct methanation system, different concentrations of this gas were tested in experiments times of 120 min. The SO₂ concentration range used of 5–100 ppm (entries 3A–3E in Table 1) was chosen based on the usual concentration of this gas on flue gas streams [30, 31].

After verifying the efficient stability of the system, several reaction sets were carried out using different pollutants (O₂—entry 2A–D, SO₂—entry 3A–G, NO—entry 4A–E). The 2A–D experiments were carried out for 120 min. with O₂ concentration between 2 and 8%, while the SO₂ experiments were carried out for 120 min. with concentrations between 5 and 100 ppm (3A–E), chosen to compare the results with data from the literature. In addition, to verify the efficiency of the catalyst in a longer exposure time with SO₂, the experiment was carried in the presence of 5 and 20 ppm, during 300 min in each concentration (3F and 3G), verifying that at 20 ppm the system already demonstrates a great decrease in efficiency. Besides that, the efficiency of the catalyst is tested with the pollutant NO (4A–D) for 120 min with each concentration (ranging between 25 and 200 ppm) and for 600 min at 100 ppm to check the behavior of the catalyst in longer times.

Product sampling and analysis

Reaction products were sampled using a simple system composed of a three-way valve and a septum. Common syringe and needle were used to sample the product gas mixture through the septum and then store it in glass vials designed for gas storage (Exetainer—Labco). Vacuum was previously made in the vials to ensure no sample contamination with air. These samples were analyzed in a gas chromatograph (Perkin Elmer—Clarus 580) with a flame ionization detector (FID) to detect the product composition in order to calculate the CO_2 conversion of each reaction. The capillary column used was the Elite Plot Q with 0.53 mm internal, 20 μm polystyrene-divinylbenzene stationary phase film thickness and 30 m in length. The temperature used in the oven was 50 °C (isothermal method). The injector and detector temperatures were 200 and 350 °C, respectively, and helium was used as the carrier gas with a flow rate of 10 mL min^{-1} . Product sampling was performed after every 30 min.

Data from product GC analysis were used to calculate carbon dioxide conversion and methane yield through Eqs. 2 and 3, respectively.

$$X_{\text{CO}_2} = 1 - \frac{[\text{CO}_2]_f}{[\text{CO}_2]_f + [\text{CO}]_f + [\text{CH}_4]_f} \quad (2)$$

$$Y_{\text{CH}_4} = \frac{[\text{CH}_4]_f}{([\text{CO}_2]_f + [\text{CO}]_f + [\text{CH}_4]_f)} \quad (3)$$

Here X_{CO_2} is the carbon dioxide conversion, Y_{CH_4} is the methane yield and $[\text{CH}_4]_f$, $[\text{CO}]_f$ and $[\text{CO}_2]_f$ are the concentrations of each element at the product stream obtained from GC analysis.

Catalyst characterization

Spent catalyst was characterized by thermogravimetric analysis (TGA, TA Instruments Q600, from room temperature to 1000 °C at a heating rate of 20 °C min^{-1} , under synthetic air atmosphere), field emission scanning electron microscopy (FESEM, FEI Inspect F50 in secondary electron beam), and transmission electron microscopy (TEM, FEI Tecnai G2T20) in order to evaluate the influence of the poisoning compounds about the same.

Results and discussion

Methanation reactions

The first set of methanation reactions was performed in order to evaluate the stability of reaction system and methods, being the results compared with literature. These first tests (Fig. 1, entries 1A and 1B) showed that the system is extremely stable for methanation since high CO₂ conversion (maintained at approximately 92%) was kept over 1530 min (or 25.5 h). These reactions were performed with proportions 4/1/5, corresponding to H₂/CO₂/N₂, simulating the average concentration of carbon dioxide in a flue gas stream. Thus, it can be claimed that inert gas does not present a negative effect over the catalyst described in the literature [32–34].

The second stage of reactions is focused on assessing the impact of pollutants (O₂, NO_x e SO_x) on the result of CO₂ conversion and selectivity in CH₄. Besides nitrogen and carbon dioxide, the oxygen is usually found at high concentration on flue gas streams. This parameter can have wide variations, but the usual values of oxygen in the flue gas vary from 2 to 8%, according to the fuel and operational parameters used [7]. According Müller et al. [7], in methanation systems, the oxygen reacts with hydrogen and causes water production, reducing the amount of hydrogen available in the system. In order to verify the influence of water formed from the existing O₂ concentration in the reaction gas stream, theoretical calculations and experiments with different amounts of O₂ were carried out in order to predict how the variation of the methanation reaction occurs. These theoretical calculations were done using Aspen Hysys (Aspentech) simulation software and experimental data are in the Table 1 (entries 2A–2D) and Fig. 2.

However, determining the amount of water formed during the reaction is quite complicated. Like this, in order to increase the proof of experimental results, the comparison made between the experimental results of the methanation reaction and

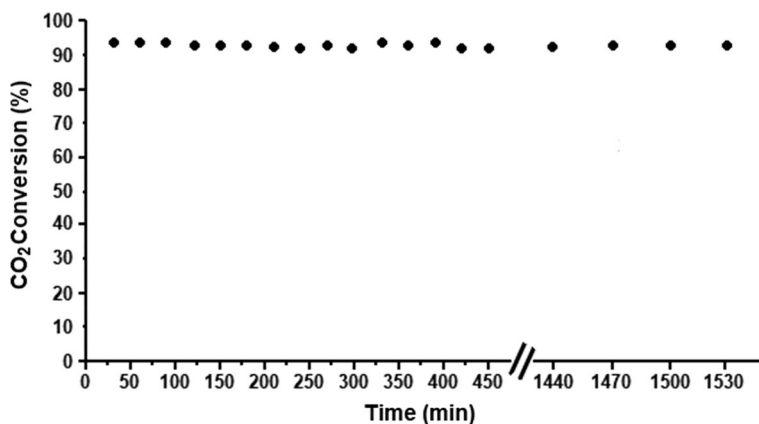
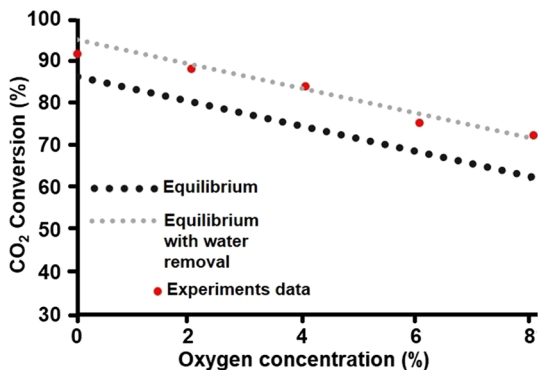


Fig. 1 Results of the reaction system stability. CO₂ Conversion obtained from methanation reaction performed at 350 °C and volumetric ratio H₂/CO₂/N₂ of 4/1/5

Fig. 2 CO₂ Conversion obtained from methanation reaction with different concentration of O₂ in flue gas (catalyst=0.4375 g, T=350 °C, volumetric ratio H₂/CO₂/N₂=4/1/5, reaction time = 120 min) Comparison between experimental data and the equilibrium data with and without water removal from the system



the theoretical results of the methanation reaction under the same experimental reaction conditions.

In the graph shown in Fig. 2, there are three plotted results. The grey and black dotted lines corresponds to the theoretical simulation of the methanation reaction with and without water removal and the red dots correspond to the experimental methanation reaction with water removal. The experimental data showed a higher similarity with the theoretical results in the methanation system with water removal, showing that theoretical calculations can be used as a parameter to predict the conversion of CO₂ in the reaction system.

The results showed that, in the reaction system studied, a decrease in the CO₂ conversion was seen with the increase in the oxygen concentration. Another aspect that corroborates with the obtained results is that the reaction of hydrogen and oxygen is even more exothermic than the formation of methane, -572 kJ/mol against -165 kJ mol^{-1} . Due to high amount of energy released, the presence of oxygen makes it harder to control the temperature increase inside the reactor, enhancing the changes of hot spot formation and catalyst sintering. Besides that, another problem related to the presence of oxygen in the system is the possibility of oxygen to react with the materials that make up the methanation system (e.g. metallic tubes (Cr–Ni alloy)) [7].

Together with these three main components of the flue gas (N₂, CO₂ and O₂), the pollutants H₂S, SO_x and NO_x form a group of elements extremely important at the direct methanation. In this way, the variation of the methanation reaction with pollutants SO₂ and NO will be shown.

Methanation reaction with SO₂

In general, sulfur is a critical element to any catalyst applied in methanation reactions, essentially due to formation of strong bound sulfur-metal [16–18]. Sulfur contamination generally occurs from the presence of H₂S or SO_x, being the SO_x the sulfured component most commonly found in flue gas flows, especially the sulfur dioxide (SO₂). Although the presence of H₂S is far more aggressive to the catalyst than SO₂, the impact of sulfur dioxide over the methanation reaction is similar to

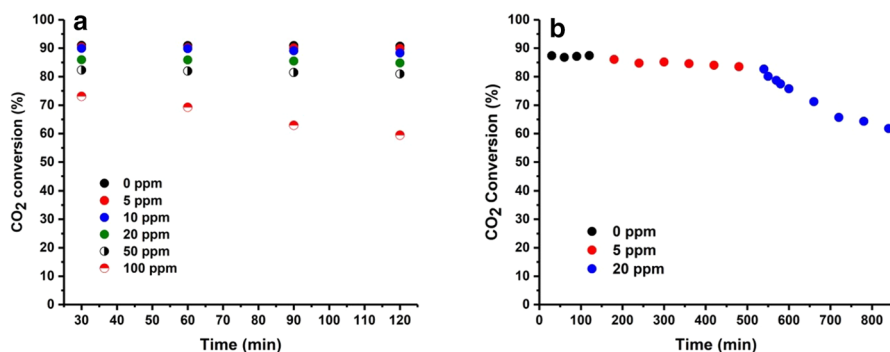


Fig. 3 CO₂ Conversion obtained from methanation reaction with different concentration of SO₂ in flue gas. **a** Short run experiments result with different SO₂ concentration (5, 10, 20, 50 and 100 ppm), showing the impact over the methanation reaction and **b** long run experiments results simulating reactions with 5 and 20 ppm of SO₂

H₂S, mostly because the first step of this reaction mechanism is the hydrogenation of SO_x to obtain the H₂S and posteriorly the attack to the catalyst, resulting in the formation of strong bounds sulfur-metal [16].

In all methanation tests (Fig. 3a), the reactions were initially carried out without SO₂ to prove the efficiency of the system, as well as serving as parameters for the results to be compared and the variation was insignificant, presenting 90% of CO₂ conversion, proving stability of the system described. With a concentration of 5 ppm SO₂, a decrease of less than 1% in the conversion of CO₂ was observed in 120 min., while in the tests carried out with 10 ppm, the variation was of 1.7%. At the concentration of 20 ppm, a 5% decrease was observed, corresponding to 85% of CO₂ conversion. This reduction in the conversion is a value considered high as the yield would be low if used in a continuous process for several hours. The following reaction carried out in concentration of 50 ppm showed another considerable decrease in the conversion (10%, that corresponding to 80% of CO₂ conversion), according to Fig. 3a.

The concentration of 100 ppm was the most critical for the reaction system. In the previous concentration (5, 10, 20 and 50 ppm of SO₂), although was observed a decrease in the CO₂ conversion, this conversion remained stable during the 120 min of each test, however, when an amount of 100 ppm SO₂ was added, the reaction system showed a wide variation at the CO₂ conversion, 80 to 71% (first 30 min.) and after 120 min to 57%. In terms of CH₄ selectivity, it remained higher than 99% for concentrations of 0, 5, 10 and 20 ppm of SO₂. However, a decrease to 80% and 65%, respectively, were observed when 50 ppm and 100 ppm of SO₂ was introduced in the system. Müller et al. [7] carried out methanation reactions in the same proportions as H₂/CO₂/N₂ (4:1:5), temperature of 350 °C, using 512 ppm SO₂ (effective 86 ppm SO₂) for 12.5 h and found that over this time the CO₂ conversion rate declined 17% (average decay rate of 1.36%/h). However, our experiments demonstrated that the influence of SO₂ can be even greater, since using lower SO₂ concentrations (20 and 50 ppm) the reduction in CO₂ conversion was higher than the reference, 5% and 10%

respectively for 2 h reaction. Comparing with the experiment using 100 ppm, the average decay rate found was even higher, reaching 27% decrease after 2 h.

In order to verify what the maximum concentration of SO₂ tolerable to obtain a good CO₂ conversion is for a longer experiment time, the methanation reaction was carried out for 6 h (Fig. 3b). The results confirmed that for 20 ppm and 6 h, the decay was 26% (a much higher value when compared to the literature [7], considering that the experiment occurred with half the reaction time). Thus, it was found that the concentration of 20 ppm SO₂ is not a viable value, because of the fast decay in catalyst efficiency. On the other hand, when the methanation reaction was carried out with 5 ppm SO₂ for 6 h, an excellent result was observed, because for 6 h the yield decay was only 3%, demonstrating that this value would be the maximum tolerable SO₂ for the methanation reaction in these conditions. This way, it is possible to propose the best working conditions in the methanation process regarding the maximum tolerable amount of SO₂ in the gas stream, without having to interrupt the process periodically, due to the low CO₂ conversion rate. The results showed that the proposed methanation reaction with 5 ppm of SO₂ has a great possibility of being applied. The 20 ppm scenario showed a reduction of 26% of the CO₂ conversion, proving that operating with a concentration as high as this would be completely impracticable.

Methanation reaction in the presence of NO

Another critical pollutant group found in flue gas streams is the NO_x. Nitrogen oxides have a significant impact on the environment when released to the atmosphere. Throughout the years, different studies tested the influence of NO₂ (used as representative substance for the NO_x group) and found no negative effect over methanation reaction [7]. However, the compositions of flue gas analyzed in previous works show that approximately only 10% of the NO_x is NO₂ and the highest amount is nitrogen monoxide (NO), close to 90% [30, 35]. At the same time, no study was found analyzing the impact of nitrogen monoxide on CO₂ methanation reaction.

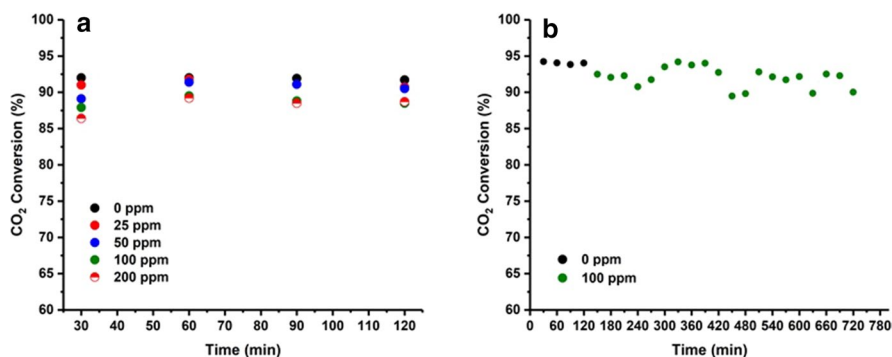


Fig. 4 CO₂ Conversion obtained from methanation reaction with different concentration of NO in flue gas. **a** Short run experiments result with different NO concentration (25, 50, 100 and 200 ppm) and **b** long run experiments results simulating reactions with 100 ppm of NO

Thus, this section of the study was dedicated to better understanding the impacts of NO presence on methanation reaction. The results of the short and long run experiments are presented on Fig. 4.

As observed in the results, the presence of the nitrogen monoxide, in all concentration, generate interferences in the reaction, which resulted in instability of the CO₂ conversion (Fig. 4a). Just in the 100 and 200 ppm concentrations, it is observed a small decrease in the CO₂ conversion (1% approximately).

Due to the reaction system showing small fluctuations in reaction yield for different concentrations of NO, it was decided to carry out a test for 12 h (720 min) with the highest concentration (100 ppm) in order to check if there is a significant influence of NO for a longer exposure time (Fig. 4b). The result shows an oscillatory profile with a decrease of up to 4.5% in methanation process yield. However, this decay was not constant. The oscillations show that the yield decreased and increased back again during the 12-h run. In the end, only a short decrease in global yield was noticed, indicating that this decay was a reversible process.

Spent catalyst

In order to evaluate the effect of poisoning compounds in the catalyst morphology and, consequently, in its catalytic activity, TEM and SEM–EDS analysis were performed. The pristine catalyst presents a clustered morphology, with larger particles related to the support (SiO₂) and smaller nickel particles (Fig. 5a). It was observed that morphology of spent catalyst (Fig. 5b) was not change when compared with pristine sample after the methanation reaction without poisoner compounds (SO₂ and NO), which led to a high and stable catalytic activity during all the tests (Fig. 1). However, after methanation reactions with poisoning compounds, as SO₂ (Fig. 3) and NO (Fig. 4) present on flue gas, a clear morphology change in spent catalyst can be noticed. The contaminant can lead to sintering of nickel particles [36] and, as observed by TEM images, these particles were separated from the support. These results go along with the catalytic activity drop found during the methanation tests observed in Fig. 3, and the oscillation observed in Fig. 4.

In order to analyze the surface composition of the catalyst, SEM–EDS analysis were performed. The Ni–SiO₂ catalyst before and after the reaction with no poisoning element (Figs. S2a and S2b), as found previously through TEM, presented a

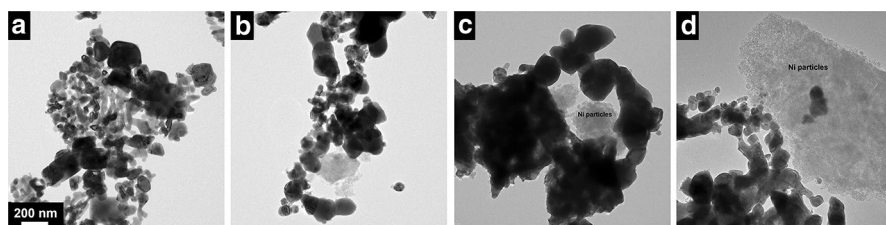


Fig. 5 Micrographs obtained by TEM of: **a** pristine catalyst, **b** spent catalyst, after use without contaminants in the flue gas, **c** spent catalyst with SO₂ as contaminant in the flue gas and **d** spent catalyst with NO as contaminant in the flue gas

similar behavior, with only a difference of small carbon formation after the experiment (Fig. 5b). In this case the carbon found in the catalyst surface is spread in a homogeneous way. On the other hand, results from catalyst after a reaction with NO showed, as seen through TEM, that the Ni particles are separated from the support. This separation results in an agglomeration process of Ni particles which enhances the carbon formation. Through the scanning shown in Fig. S2c it is possible to notice a higher carbon concentration on these agglomerated pure Ni particles.

The reactions with SO₂ as pollutant, although presented a similar result to reaction with NO on TEM analysis, when studied through SEM differences could be found. The damage caused to the catalyst was superior when exposed to SO₂ environment, ripping apart the Ni particles from the support. Fig. S3d shows the support areas with pure Si, characteristic element of the support. Fig. S3e, on the other hand, shows a structure of pure agglomerated Ni, as shown through the EDS scanning image.

Sulfur presence, even in small concentrations (10 ppm or less) may be enough to poison a nickel catalyst [37]. Sulfur interact with nickel surface covering the particles which will lead to the deactivation [38]. In our work, its observed that this interaction its associated with a geometric effect more than an electronic effect, where the surface sites active are blocked by sulfur poisoning, according with literature [39]. The results obtained in long run experiments (Fig. 3b) showed that when 20 ppm of SO₂ is introduced, it observed a significative decrease in the CH₄ yield which can attributed to the crucial point of the deactivation. The interaction of sulfur and Ni particles causes the sintering [40], forming NiS_x species that, as showed by SEM–EDS analysis, will lead to the ripping of Ni particles.

TGA analysis of the spent catalyst, *i.e.* without contaminant, with SO₂ and with NO are presented in Fig. S4. As observed, the three catalysts profile in temperatures below 200 °C presented a slight weight loss that can be related to the loss of adsorbed gas and surface water [41], being higher to catalyst with contaminants (SO₂ and NO ≈ 5%). The higher weight loss between 200 and 400 °C can be related to the oxidation of Ni⁰ to NiO [42]. Above 600 °C, a weight loss was observed, which was ascribed to the oxidation of deposited inert carbon [43]. In EDS analysis, carbon deposition was not observed when SO₂ was used, however, by TGA its clear that, in the presence of this contaminant, there is a deposition of carbon and it is higher than reactions with NO.

Conclusions

The stability tests of methanation reaction with N₂:CO₂:H₂ presented similar results to the literature, validating the system developed for carbon dioxide catalytic conversion. Although nitrogen did not present a negative impact over methanation reaction, experiments with the presence of the oxygen showed that the O₂ consumes the hydrogen and produces more water, reducing the CO₂ conversion and CH₄ formation. On the same side, the sulfur dioxide (SO₂) also had a negative impact on the reaction performance. Different from the oxygen, this pollutant attacked the catalyst surface separating the nickel particles from the support and

changing the catalyst morphology. The results of this work show that the methanation process can be carried out with a maximum of 5 ppm SO₂, without obtaining significant losses in the conversion rate from CO₂ to methane.

Although the NO can be considered poisoning elements to the catalyst, its presence did not present a significant decay on catalyst efficiency as SO₂. On the other hand, the presence of nitric oxide showed an anomalous behaviour of the catalyst, requiring more studies on the mechanism that could explain the interaction of this gas with the catalyst surface.

SEM analysis showed that the catalyst deactivation could be related to changes in its morphology. Nitric oxide presence, which showed a smaller reduction on catalytic activity, resulted in Ni particle agglomeration followed by carbon deposition over these clusters. More harmful to the reaction than NO, the presence of SO₂ in the feed stream ripped off the nickel particles from the support resulting in the accelerated decrease in catalytic activity. TGA analysis showed that the carbon formation is more significant in experiments with SO₂ as poisoning agent.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11144-021-02092-8>.

Acknowledgements The authors would like to thank the National Research Council (CNPq) and the Pontifical Catholic University of Rio Grande do Sul (PUCRS) for technical support, and the Central Laboratory of Microscopy and Microanalysis (LabCEMM/PUCRS) for the morphological analyses.

References

1. Koschany F, Schlereth D, Hinrichsen O (2016) On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)_x. *Appl Catal B Environ* 181:504–516. <https://doi.org/10.1016/j.apcatb.2015.07.026>
2. Stangeland K, Kalai D, Li H, Yu Z (2017) CO₂ methanation: the effect of catalysts and reaction conditions. *Energy Procedia* 105:2022–2027. <https://doi.org/10.1016/j.egypro.2017.03.577>
3. Vieira MO, Monteiro WF, Neto BS et al (2019) Chemical fixation of CO₂: the influence of linear amphiphilic anions on surface active ionic liquids (SAILs) as catalysts for synthesis of cyclic carbonates under solvent-free conditions. *React Kinet Mech Cat* 126:987–1001. <https://doi.org/10.1007/s11144-019-01544-6>
4. (2018) MAHA ENERGY AB Annual Report
5. Yen HW, Ho SH, Chen CY, Chang JS (2015) CO₂, NO_x and SO_x removal from flue gas via microalgae cultivation: a critical review. *Biotechnol J* 10:829–839. <https://doi.org/10.1002/biot.201400707>
6. Monteiro WF, Vieira MO, Calgaro CO et al (2019) Dry reforming of methane using modified sodium and protonated titanate nanotube catalysts. *Fuel* 253:713–721. <https://doi.org/10.1016/j.fuel.2019.05.019>
7. Müller K, Fleige M, Rachow F, Schmeißer D (2013) Sabatier based CO₂-methanation of flue gas emitted by conventional power plants. *Energy Procedia* 40:240–248. <https://doi.org/10.1016/j.egypro.2013.08.028>
8. Rönsch S, Schneider J, Matthischke S et al (2016) Review on methanation: from fundamentals to current projects. *Fuel* 166:276–296. <https://doi.org/10.1016/j.fuel.2015.10.111>
9. Rönsch S, Köchermann J, Schneider J, Matthischke S (2016) Global reaction kinetics of CO and CO₂ methanation for dynamic process modeling. *Chem Eng Technol* 39:208–218. <https://doi.org/10.1002/ceat.201500327>

10. Xu L, Wen X, Chen M et al (2020) Mesoporous Ce-Zr solid solutions supported Ni-based catalysts for low-temperature CO₂ methanation by tuning the reaction intermediates. *Fuel* 282:118813. <https://doi.org/10.1016/j.fuel.2020.118813>
11. Lv C, Xu L, Chen M et al (2020) Constructing highly dispersed Ni based catalysts supported on fibrous silica nanosphere for low-temperature CO₂ methanation. *Fuel* 278:118333. <https://doi.org/10.1016/j.fuel.2020.118333>
12. Loder A, Siebenhofer M, Lux S (2020) The reaction kinetics of CO₂ methanation on a bifunctional Ni/MgO catalyst. *J Ind Eng Chem* 85:196–207. <https://doi.org/10.1016/j.jiec.2020.02.001>
13. Abelló S, Berruero C, Montané D (2013) High-loaded nickel-alumina catalyst for direct CO₂ hydrogenation into synthetic natural gas (SNG). *Fuel* 113:598–609. <https://doi.org/10.1016/j.fuel.2013.06.012>
14. Becker WL, Penev M, Braun RJ (2018) Production of synthetic natural gas from carbon dioxide and renewably generated hydrogen: a techno-economic analysis of a power-to-gas strategy. *J Energy Resour Technol Trans ASME*. <https://doi.org/10.1115/1.4041381>
15. Ghaib K, Ben-Fares FZ (2018) Power-to-methane: a state-of-the-art review. *Renew Sustain Energy Rev* 81:433–446. <https://doi.org/10.1016/j.rser.2017.08.004>
16. Baraj E, Snajdrova V, Hlincik T, Ciahotny K (2016) The influence of sulphur dioxide on the methanation activity of a nickel based catalyst. *Int J Adv Sci* 4:125–128
17. Czekaj I, Struis R, Wambach J, Biollaz S (2011) Sulphur poisoning of Ni catalysts used in the SNG production from biomass: computational studies. *Catal Today* 176:429–432. <https://doi.org/10.1016/j.cattod.2010.10.078>
18. Bartholomew CH, Weatherbee GD, Jarvi GA (1979) Sulfur poisoning of nickel methanation catalysts. I. In situ deactivation by H₂S of nickel and nickel bimetallics. *J Catal* 60:257–269. [https://doi.org/10.1016/0021-9517\(79\)90147-7](https://doi.org/10.1016/0021-9517(79)90147-7)
19. Toemen S, Bakar WAWA, Ali R (2014) Copper/nickel/manganese doped cerium oxides based catalysts for hydrogenation of CO₂. *Bull Korean Chem Soc* 35:2349–2356. <https://doi.org/10.5012/bkcs.2014.35.8.2349>
20. Hausberger AL, Atwood K, Knight CB (1975) Development of methanation catalysts for synthetic natural gas processes. *Am Chem Soc*. <https://doi.org/10.1021/ba-1975-0146.ch003>
21. Castellani B, Gambelli AM, Morini E et al (2017) Experimental investigation on CO₂ methanation process for solar energy storage compared to CO₂-based methanol synthesis. *Energies* 10:1–13. <https://doi.org/10.3390/en10070855>
22. Danaci S, Protasova L, Lefevre J et al (2016) Efficient CO₂ methanation over Ni/Al₂O₃ coated structured catalysts. *Catal Today* 273:234–243. <https://doi.org/10.1016/j.cattod.2016.04.019>
23. He B, Zhao Q, Zeng Z et al (2015) Effect of hydrothermal reaction time and calcination temperature on properties of Au@CeO₂ core-shell catalyst for CO oxidation at low temperature. *J Mater Sci* 50:6339–6348. <https://doi.org/10.1007/s10853-015-9181-z>
24. Ahmad W, Al-Matar A, Shawabkeh R, Rana A (2016) An experimental and thermodynamic study for conversion of CO₂ to CO and methane over Cu-K/Al₂O₃. *J Environ Chem Eng* 4:2725–2735. <https://doi.org/10.1016/j.jece.2016.05.019>
25. Falcinelli S, Capriccioli A, Pirani F et al (2017) Methane production by CO₂ hydrogenation reaction with and without solid phase catalysis. *Fuel* 209:802–811. <https://doi.org/10.1016/j.fuel.2017.07.109>
26. Granitsiotis G (2017) Methanation of carbon dioxide experimental research of separation enhanced methanation of CO₂. Delft University of Technology
27. Lazdans A, Dace E, Gusca J (2016) Development of the experimental scheme for methanation process. *Energy Procedia* 95:540–545. <https://doi.org/10.1016/j.egypro.2016.09.082>
28. Wang S, Schruk ET, Mahajan H, Farrauto RJ (2017) The role of ruthenium in CO₂ capture and catalytic conversion to fuel by dual function materials (DFM). *Catalysts* 7:1–13. <https://doi.org/10.3390/catal7030088>
29. Lars J, Ehimen EA, Born JBH-N (2015) Dynamic biogas upgrading based on the Sabatier process: thermodynamic and dynamic process simulation. *Bioresour Technol* 178:323–329. <https://doi.org/10.1016/j.biortech.2014.10.069>
30. Chapel DG, Mariz CL, Ernest J (1999) Recovery of CO₂ from flue gases : commercial trends. *Can Soc Chem Eng Annu Meet*. <https://doi.org/10.1016/j.apenergy.2013.03.089>
31. Onarheim K, Santos S, Kangas P, Hankalin V (2017) Performance and costs of CCS in the pulp and paper industry part 1: performance of amine-based post-combustion CO₂ capture. *Int J Greenh Gas Control* 59:58–73. <https://doi.org/10.1016/j.ijggc.2017.02.008>

32. Kiendl I, Klemm M, Clemens A, Herrman A (2014) Dilute gas methanation of synthesis gas from biomass gasification. *Fuel* 123:211–217. <https://doi.org/10.1016/j.fuel.2014.01.036>
33. Matthischke S, Krüger R, Rönsch S, Güttel R (2016) Unsteady-state methanation of carbon dioxide in a fixed-bed recycle reactor: experimental results for transient flow rate ramps. *Fuel Process Technol* 153:87–93. <https://doi.org/10.1016/j.fuproc.2016.07.021>
34. Miguel CV, Mendes A, Madeira LM (2018) Intrinsic kinetics of CO₂ methanation over an industrial nickel-based catalyst. *J CO₂ Util* 25:128–136. <https://doi.org/10.1016/j.jcou.2018.03.011>
35. Vakkilainen E (2005) Kraft recovery boilers: principles and practice, 2nd ed
36. Miao B, Ma SSK, Wang X et al (2016) Catalysis mechanisms of CO₂ and CO methanation. *Catal Sci Technol* 6:4048–4058. <https://doi.org/10.1039/c6cy00478d>
37. Struis RPWJ, Schildhauer TJ, Czekaj I et al (2009) Sulphur poisoning of Ni catalysts in the SNG production from biomass: a TPO/XPS/XAS study. *Appl Catal A Gen* 362:121–128. <https://doi.org/10.1016/j.apcata.2009.04.030>
38. Legras B, Ordonsky VV, Dujardin C et al (2014) Impact and detailed action of sulfur in syngas on methane synthesis on ni/γ-Al₂O₃ catalyst. *ACS Catal* 4:2785–2791. <https://doi.org/10.1021/cs500436f>
39. Agrawal PK, Katzer JR, Manogue WH (1982) Methanation over transition-metal catalysts. *J Catal* 74:332–342
40. Yuan C, Yao N, Wang X et al (2015) The SiO₂ supported bimetallic Ni-Ru particles: a good sulfur-tolerant catalyst for methanation reaction. *Chem Eng J* 260:1–10. <https://doi.org/10.1016/j.cej.2014.08.079>
41. Chen X, Jiang J, Yan F et al (2017) Dry reforming of model biogas on a Ni/SiO₂ catalyst: overall performance and mechanisms of sulfur poisoning and regeneration. *ACS Sustain Chem Eng* 5:10248–10257. <https://doi.org/10.1021/acssuschemeng.7b02251>
42. Li X, Li D, Tian H et al (2017) Dry reforming of methane over Ni/La₂O₃ nanorod catalysts with stabilized Ni nanoparticles. *Appl Catal B Environ* 202:683–694. <https://doi.org/10.1016/j.apcatb.2016.09.071>
43. Zhao J, Zhou W, Ma J (2014) Pretreatment as the crucial step for biogas reforming over Ni-Co bimetallic catalyst: a mechanistic study of CO₂ pretreatment. *Int J Hydrogen Energy* 39:13429–13436. <https://doi.org/10.1016/j.ijhydene.2014.04.021>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.