Syngas production via microwave-assisted dry reforming of methane

de Dios García, Ignacio; Stankiewicz, Andrzej; Nigar, Hakan

DOI
10.1016/j.cattod.2020.04.045

Publication date
2021

Document Version
Final published version

Published in
Catalysis Today

Citation (APA)
de Dios García, I., Stankiewicz, A., & Nigar, H. (2021). Syngas production via microwave-assisted dry reforming of methane. *Catalysis Today*, *362*, 72-80. https://doi.org/10.1016/j.cattod.2020.04.045

Catalysis Today 362 (2021) 72–80

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Syngas production *via* microwave-assisted dry reforming of methane

Ignacio de Dios García, Andrzej Stankiewicz, Hakan Nigar*

Process & Energy Department, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, the Netherlands

ARTICLE INFO

Keywords:
Heterogeneous catalysis
Microwave heating
Dry reforming
Syngas
Methane
Carbon dioxide

ABSTRACT

Energy-efficient CH_4-CO_2 valorization to fuels and chemicals presents an urgent need considering the great variety of methane sources and the removal of greenhouse gases. In the present work, the microwave-assisted dry reforming of methane, DRM, has been carried out in a custom-designed rectangular mono-mode microwave applicator over several catalyst-support combinations, *i.e.*, Pt/C, Ni/Al_2O_3, mechanical mixture of Ni/Al_2O_3-SiC and Ni/SiC. The high and steady conversions of CH_4 and CO_2 were obtained in the case of the mechanical mixture of Ni/Al_2O_3-SiC and Ni/SiC. In all the combinations investigated, the conversions reached up to 90% at a WHSV of 11,000 mL/g/h, and microwave power input of 45–60 W, at 800 °C. No significant catalyst deactivation has been observed during the 6-h operation except of Pt/C catalyst. Moreover, the microwave-assisted dry reforming of methane over Ni/SiC was shown to be an interesting, cheap process candidate, able to compete with the steam reforming.

1. Introduction

Sustainable development in chemical processes includes the utilization of renewable energy resources. Unfortunately, fossil-based fuels are still the dominant primary source of energy. Our dependency on the fossil fuels increases the anthropogenic emission of carbon dioxide, which is the major part of the greenhouse gases [1]. The global carbon dioxide concentration in the atmosphere has already surpassed 400 ppm according to the recent data from the Earth System Research Laboratory (ESRL) at the National Oceanic & Atmospheric Administration (NOAA) [2]. The report of the Intergovernmental Panel on Climate Change (IPCC, 4th assessment report 2016), declares the safe level of CO_2 concentration to be below 350 ppm.

Dry reforming of methane (DRM, reaction (1)) presents one of possible ways to valorize CO_2 and convert it to a useful product: the synthesis gas also known as syngas. Compared to other methods for making syngas from methane (steam reforming or partial oxidation), DRM offers lower production ratio of H_2 and CO. This is beneficial for the production of liquid hydrocarbons, considering the subsequent treatment of syngas, *via* Fischer–Tropsch synthesis.

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO\Delta H_{298} = +247\,\mathrm{kJ/mol} \tag{1}$$

Nevertheless, due to the high thermal stabilities of CH_4 and CO_2 (high bond-dissociation energies of $CH_3{-}H$ and $C{=}O{-}O$ are 435 and 532 kJ/mol, respectively), the DRM presents a difficult, highly endothermic process. It requires high operating temperatures, *e.g.*, 700–1000 °C, and low pressures to reach desirable conversion levels of CH_4 and CO_2[3–6]. Nikoo et al. [7] studied the thermodynamics of DRM focusing on the aspect of carbon formation. They state that DRM reaction to form syngas is the favored reaction, particularly at a temperature above 727 °C. That reaction is typically accompanied by the simultaneous reverse water-gas shift reaction (RWGS, reaction (2)). On the other hand, there are important side reactions which are responsible for the carbon deposition and affect the production ratio of H_2 and CO_2, such as methane decomposition (reaction (3)) and carbon dioxide disproportionation, the so-called Boudouard reaction (reaction (4)). At higher temperatures, reaction (3) is more likely responsible for the carbon formation and reaction (4) tends to occur below 527 °C and can be influenced by equilibrium limitations at the higher temperature [7].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O\Delta H_{298} = +41\,\mathrm{kJ/mol} \tag{2}$$

$$CH_4 \rightleftharpoons C + 2H_2\,\Delta H_{298} = +75\,\mathrm{kJ/mol} \tag{3}$$

$$2\,CO \rightleftharpoons C + CO_2\,\Delta H_{298} = -173\,\mathrm{kJ/mol} \tag{4}$$

A variety of metal-based catalysts, including noble (Pt, Pd, Rh, Ru, and Ir) and transition metals (Co, Ni, and Fe), have been studied in the DRM reaction [4,8,9]. Ni-based catalysts are one of the most frequently studied transition metal catalysts, due to their high reactivity with methane, low-cost and large abundance. However, thermodynamically inevitable carbon deposition on active surfaces of Ni decreases the performance of the catalyst during the process [10,11].

The DRM is an energy demanding but environmentally important

---

* Corresponding author.
E-mail address: h.nigar@tudelft.nl (H. Nigar).

https://doi.org/10.1016/j.cattod.2020.04.045
Received 28 November 2019; Received in revised form 17 March 2020; Accepted 22 April 2020

process. Conventional electrical heating is the most widely used energy source in the studies of DRM. However, supplying the required heat with conventional heating is challenging and energetically inefficient, since the whole system including gas streams must be heated. On the other hand, microwave-susceptible catalysts and/or catalyst supports can be selectively heated by microwaves in an energy-efficient way. Microwave-assisted reactor concepts can reduce the energy consumption considerably. Moreover, quick start and stop possibility and gas-solid temperature difference due to the selective heating can reduce the unwanted side reactions [12,13].

Different Ni-based catalysts have been investigated in DRM process under conventional thermal heating [14–17]. Recently, Wang et al. [14] developed a nanostructured Ni-based catalyst supported on spinel, $MgAl_2O_4$. They observed high catalytic activity; the conversion of CH_4 and CO_2 at 900 °C with a reached 87 and 91%, respectively (CO_2:CH_4:N_2 = 1:1:2, WHSV = 912,000 mL/g/h, 5 wt% Ni, 76 kPa). Ma et al. [16] developed nickel-based mesoporous alumina (Ni-MA) catalyst *via* the one-step evaporation-induced self-assembly (EISA) method. The Ni-MA catalyst showed 93% conversions of CH_4 and CO_2 at 800 °C (CO_2:CH_4:1, WHSV = 24,000 mL/g/h, 6 wt% Ni, 101 kPa). Moreover, Wei et al. [17] studied Ni impregnated SiC (Ni/SiC-IMP) prepared by EISA method and Ni/Al_2O_3 as reference catalysts in their work on DRM process. However, the catalysts activities were relatively low and the conversions of CH_4 and CO_2 at 750 °C were 15–20% and 30–35%, respectively, (CO_2:CH_4:1, WHSV = 15,000 mL/g/h, 2 wt% Ni, 101 kPa).

The microwave heating mechanism changes depending on the composition of the materials. In this regard, the proper material selection is crucial. If the material of interest is not/or moderate microwave-susceptible, a mixture of this material with microwave-susceptible materials, *e.g.*, silicon carbide (SiC) and carbon, can be prepared in order to reach the desired reaction temperature. The detailed information on the interaction between microwaves and solid materials can be found elsewhere [18–20].

Several researchers have performed the DRM reaction under microwave heating [21–24]. Fidalgo et al. [21] studied microwave-assisted dry reforming of methane over activated carbon. Here, activated carbon acted as catalyst and microwave-susceptible material. The DRM reaction accompanied by simultaneous CO_2 gasification of carbon reaction ($C + CO_2 \rightleftharpoons CO$) was carried out at temperatures 700–800 °C. After 6 h operation (CH_4:CO_2 = 1, WHSV = 320 mL/g/h, 800 °C), the conversions of $CH_4$and CO_2 dropped by 20% and 30%, respectively. This was due to the non-recovered active centers of Ni catalyst during the DRM process. Fidalgo et al. also observed that CO_2 gasification of carbon support was more pronounced in the microwave heating. This was confirmed by the weight loss of the catalytic bed, *in situ* carbon gasification with CO_2. The same group [23] also studied the Ni/Al_2O_3 catalyst in the microwave-assisted dry reforming of methane. Due to the low microwave-susceptibility of Ni/Al_2O_3 catalyst itself, the group prepared a mechanical mixture of Ni/Al_2O_3 with a microwave-susceptive material – carbon. The addition of carbon improved both the heating of the fixed-bed and conversions of CH_4 and CO_2. One can therefore speak about carbon bi-functionality in the system, as a microwave-susceptible material and as a catalyst.

Recently, Gangurde et al. [25] synthesized a ruthenium-doped $SrTiO_3$ perovskite catalyst and applied it in the DRM reaction. The synthesized $Ru/SrTiO_3$ showed high microwave susceptibility and stable catalytic behavior. As a continuation, the same group [26] studied a range of mechanical mixtures of $Ru/SrTiO_3$ and different commercial and relatively cheap nickel supported metal oxides, in order to improve the overall microwave heating properties. In this work, we studied microwave-assisted DRM on Pt/C and Ni/Al_2O_3 catalysts, and two silicon carbide-based mechanical mixtures, *i.e.* Ni/Al_2O_3-SiC and Ni/SiC. The above catalysts were tested under varying microwave power, different CH_4:CO_2 vol% feed ratios and space velocities in order to determine the best candidate and optimum operating conditions.

2. Experimental

2.1. Materials and preparations

In this study, commercial SiC (SiCat, Germany), Pt/C (Sigma-Aldrich), Ni/Al_2O_3, (10 wt% Ni) (Johnson Matthey, UK) and the in-lab prepared Ni-impregnated SiC (denoted as Ni/SiC) were used. The Ni (10 wt%) impregnation on SiC was performed through an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$. SiC, as microwave-susceptible support, was soaked in the solution for one day at room temperature, and dried in an oven at 120 °C in air. Then, the catalysts were calcined in a muffle furnace at 500 °C for 5 h. In order to prevent compaction of the fixed-bed, the fine powders of all aforementioned materials, were first pelletized, and then crushed and ground to 250–480 μm. Mechanical mixtures of the Ni/Al_2O_3 and SiC were prepared with a weight ratio of 1:1. The prepared mixtures were then directly used in the reaction tests without any further pretreatment.

2.2. Microwave heating system

A custom-designed mono-mode microwave applicator (SAIREM), previously described in [25,27], includes a solid-state microwave generator with the maximum power of 400 W. The microwave generator operates at the spectral band of 2.4–2.5 GHz, which enables the fine-tuning by changing the microwave field frequency in the available 100 MHz range, in increments of 0.1 MHz. Rectangular air-filled aluminum waveguides (WR340) support the TE_{10} mode. The microwave applicator also includes three sliding short circuits (SAIREM) to adjust the resonant frequency of the mono-mode cavity. Prior to the start of each experiment, the sliding short circuits were set manually to minimize the microwave reflection (lower than 10% of the forward power). For this purpose, the network analyzer (Agilent ENA series E5071) was employed [28–30] to measure reflected power within the frequency range of 2.4–2.5 GHz with 0.1 MHz steps. Once the optimum frequency was determined, the microwave generator was connected to the applicator.

2.3. Temperature measurements

The temperature measurement in microwave heating systems presents a challenging task. Thermocouples cannot be used because they interfere the microwave field. Since DRM reaction takes place at elevated temperatures, *i.e.*, 600–800 °C, optical fiber sensors also cannot be employed due to the temperature limitations (usually circa 250 °C for the commercial sensors). Therefore, non-contact temperature measurement techniques, *e.g.*, infrared thermal cameras, have to be applied. In this work, two different types of infrared thermal cameras were used for the temperature measurements – see Table 1. The accuracy of the measurement was ± 2 °C or ± 2% of the reading. After reaching the steady-state temperature, the average temperature of the area occupied by the catalyst was calculated from the outer surface temperature of the quartz reactor, using the software of the cameras.

2.4. Thermal stability and catalytic performance tests

Thermal stability tests of the materials were performed with microwave heating at 800 °C and 120 mL/min N_2 flow for 6 h, under atmospheric pressure, using a quartz tube (8 mm in diameter) filled with

Table 1
Characteristics of infrared cameras.

Camera	Temperature range (°C)	Optical spectral range (μm)
FLIR, A655sc	− 40 to 2000	7.5–14
OPTRIS PI 1M	450–1800	0.85–1.1

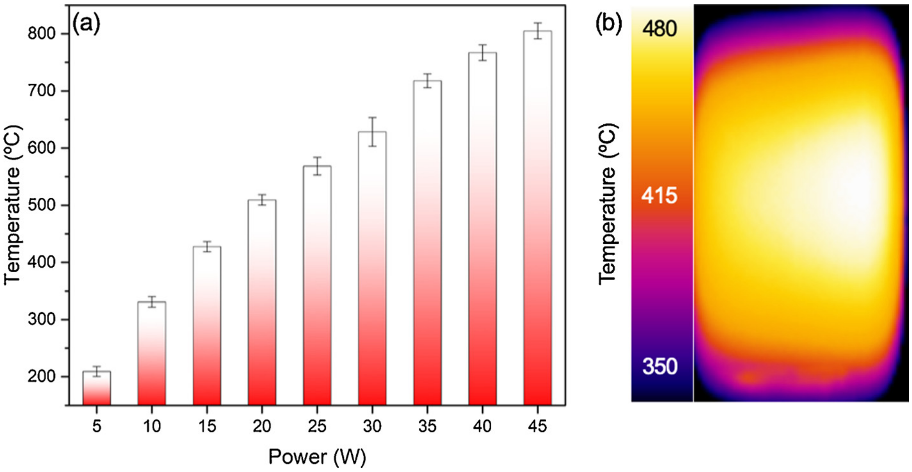

Fig. 1. (a) Heating test of Pt/C under a flow of 100 mL/min N_2. (b) Temperature distribution of Pt/C on the quartz reactor at 15 W.

the fixed-bed (catalyst particle diameter = 250–480 µm, length = 15 mm). Then, selected materials were tested on catalytic performance in the DRM process. Due to the lack of autonomous control and restricted working hours in our laboratory, the catalytic performance trials were run for maximum 6 h. To perform a standard test, the equimolar mixture of CH_4 and CO_2 with a total flow of 100 mL/min (WHSV of 11,000 mL/g/h) was fed to the reactor. The concentration changes of the reactants and products (CH_4, CO_2, H_2, and CO) were measured with the gas chromatograph (Agilent 7890B GC System).

3. Results and discussions

3.1. Thermal stability and catalytic performance tests

3.1.1. Platinum on carbon, Pt/C

Thermal stability of the Pt/C catalyst was studied under different microwave power inputs. The test was performed with three different batches of the catalyst and repeated three times per batch. Each experiment was carried out under a flow of 100 mL/min N_2, while the microwave input power was increased until the required DRM reaction temperatures, *e.g.*, 600, 700 and 800 °C were reached. Fig. 1 shows the surface temperatures of the quartz reactor wall at different microwave power inputs measured by the infrared thermal camera (FLIR, A655sc).

The desired temperatures of 600, 700 and 800 °C were reached with a 30, 35 and 45 W microwave power inputs, respectively, see Fig. 1(a). Reproducible heating results were obtained; however, the overall catalytic bed temperature distribution was not homogeneous, see Fig. 1(b). The right side of the catalytic bed had higher temperature than the rest of the catalytic area. This is due to the electromagnetic field distribution inside the microwave cavity as well as Pt/C catalytic bed. The electromagnetic field distribution is directly related to the dielectric properties of the material under test. This non-homogenous temperature distribution was explained in detail in the previous studies *via* experimental and numerical analysis [30]. Shortly speaking, the high-values of dielectric constant and loss factor affected significantly the electric field distribution inside the microwave cavity. Hence, the highest electric field intensity of the standing wave and consequently highest temperatures were located in the right part of the fixed-bed.

The performance of the Pt/C catalyst was tested with a CH_4/CO_2 feed ratio of 1 at different temperatures, *i.e.*, 600, 700 and 800 °C at a WHSV of 11000 mL/g/h. Three different batches were prepared and tested for the three temperatures in order to ensure the reproducibility of the test. The conversions of CH_4 and CO_2 at different temperatures and corresponding ratios of H_2/CO and supplied power inputs are presented in Fig. 2.

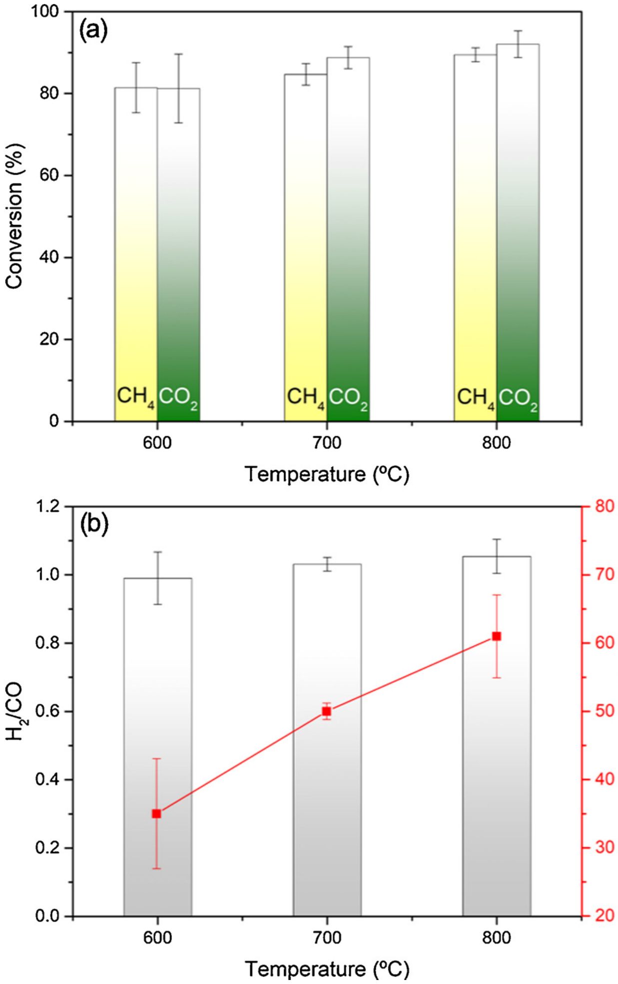

Fig. 2. Catalytic performance of Pt/C at 600, 700 and 800 °C in terms of (a) CH_4 and CO_2 conversions (b) H_2/CO ratios and supplied microwave power inputs.

It is clear that both conversions of CH_4 and CO_2 increase with temperature. In particular, at 600 °C the conversions of CH_4 and CO_2 were similar, see Fig. 2(a). However, at higher temperatures the conversion of CO_2 is slightly higher than CH_4. Similar behavior reported by Fidalgo et al. [21], where a 10% difference between CO_2 and CH_4 conversions was observed at 800 °C, 320 mL/g/h, after 5 h. The described difference can be caused by either (i) catalyst deactivation which reduces the CH_4 conversion or (ii) *in situ* carbon gasification

($C+ CO_2 \rightleftharpoons CO$) from carbon support or (iii) carbon deposition *via* CH_4 decomposition ($CH_4 \rightleftharpoons C+ 2H_2$) and/or Boudouard reaction ($CO \rightleftharpoons C+ CO_2$). The ratios of H_2 and CO in the product gas are close to 1 at the three temperatures concerned, see Fig. 2(b). The large error bars in the conversion of CH_4 and CO_2 and the ratios of H_2 and CO, especially at 600 and 800 °C, can be explained by the continuous fluctuation in the supplied microwave power, see Fig. 2(b). For example, in order to keep the temperature at 600 °C, the supplied microwave power needed to be continuously reduced. This effect could be explained by the carbon deposition at 600 °C being higher than its *in situ* consumption. This is because the carbon formation through the Boudouard reaction ($2\ CO \rightleftharpoons C+ CO_2$), the hydrogenation of carbon monoxide ($CO+ H_2 \rightleftharpoons C+ H_2O$), and the hydrogenation of carbon dioxide ($CO_2 + 2H_2 \rightleftharpoons C+ 2H_2O$) reactions are favored at lower temperature (527 °C) [7]. One has to remember that carbon is a good microwave absorbing material. Hence, the temperature increases with carbon deposition at the constant supplied microwave power. On the other hand, the effect was the opposite at 800 °C. In this case, the supplied microwave power had to be increased, in order to keep the temperature at 800 °C. This is mainly due to the *in situ* carbon gasification with CO_2, which results in an increase in the required power at 800 °C. The temperature was roughly constant for 1-h test at 700 °C. This is mainly because the both aforementioned effects are roughly compensated at this temperature.

Wang et al. [31] stated that the decomposition of CH_4 happens above 557 °C, while the disproportionation of CO ($2\ CO \rightleftharpoons C+ CO_2$) below 700 °C. The deposition of carbon generated hot spots in different areas of the catalytic fixed-bed. Due to the lack of uniformity in the temperature distribution, the production of carbon will be higher in the areas with lower temperatures [31,32]. Furthermore, the reduction on the catalytic-bed volume was observed after the DRM experiments. It was difficult to measure the weight-loss due to the problems associated with removing the catalyst from the quartz reactor. The variation in the catalytic volume might indicate that carbon of the catalyst was reacted. Both factors generate a change in the heating pattern.

In order to determine the catalyst stability, a 6-h test at 700 °C (CO_2:CH_4 = 1, WHSV = 5500 mL/g/h, 101 kPa) was performed to evaluate the conversion loss with time. The conversions of CH_4 and CO_2, the ratios of H_2/CO and the supplied microwave power are presented in Fig. 3. The first two hours presented similar conversions for CH_4 and CO_2. However, both conversions of CH_4 and CO_2 started to decrease and differ from each other for the rest of the experiment (CH_4: from 87% to 70%, and CO_2: from 86% to 74%), see Fig. 3(a). This result might mean that the non-homogeneous carbon formation can generate a significant deactivation of Pt catalyst. Moreover, a side reaction may take place in between the produced carbon and CO_2 *via in situ* carbon gasification, $C+ CO_2 \leftrightarrow 2CO$, which results in higher CO_2 conversions. This result can be also observed in Fig. 3(b) due to the reduction in the H_2/CO ratio which might indicate that more CO was produced. In terms of the supplied microwave power input (see Fig. 3(b)) a slight decrease over the studied period is observed. This is because the less conversion of CH_4 and CO_2 requires less energy input. In the work of Fidalgo et al. [21], the conversions of CH_4 and CO_2 dropped drastically to 40 and 45%, respectively, at the same condition with a lower space velocity (CO_2:CH_4 = 1, WHSV = 920 mL/g/h, activated carbon: Filtracarb FY5). It should be also highlighted that different kind of carbon formation during DRM process can play a significant role [33]. On one hand, the deposited carbon acts as a microwave absorbing medium, which leads to the power reduction. On the other hand, more active carbon can be simultaneously consumed in the process *via* carbon gasification with CO_2.

3.1.2. Nickel on alumina, Ni/Al_2O_3

Nickel supported catalysts are widely used for the DRM reaction as alternative to noble metals supported catalysts, and this is mostly due to their high activity, availability and low cost [23,34]. For that reason, we subjected this catalyst to the microwave heating test, during which the temperature linearly increased with increasing microwave power inputs (data not shown). Unfortunately, even with the maximum microwave power input, *i.e.* 400 W, the achieved temperature was circa 400 °C, which is far from the temperature levels required to perform the DRM reaction. This is due to poor dielectric properties of the Al_2O_3 support, which make it slightly microwave-transparent. Higher temperatures can be achieved with higher microwave power input because the dielectric loss of the Al_2O_3 support increases with temperature from 0.06 to 0.2 linearly between 250–600 °C [35] but these temperatures are still not enough to run the DRM reactions. Therefore, a mixture of Ni/Al_2O_3 with a microwave-susceptible material, *e.g.*, silicon carbide, must be used in order to reach the desired operating conditions for the DRM, *i.e.* 600–800 °C. Similar conclusion was achieved by Fidalgo et al. [23].

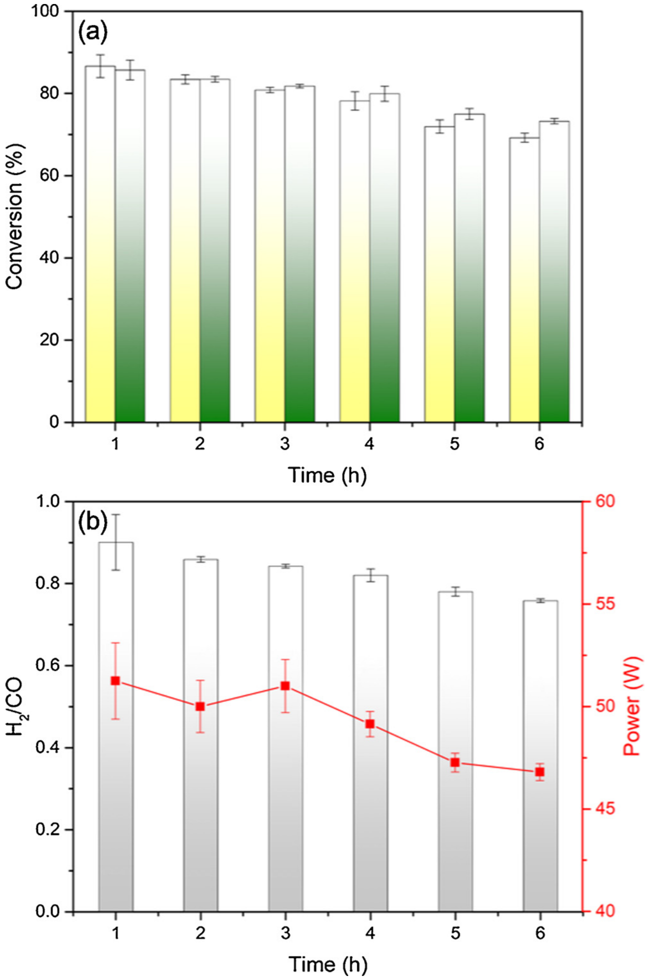

Fig. 3. Stability test of Pt/C at 700 °C in terms of (a) CH_4 and CO_2 conversions (b) H_2/CO ratios and supplied microwave power inputs.

3.1.3. Mixture of Ni/Al_2O_3 and different SiC polytypes

Silicon carbide, SiC, is a good candidate as a catalyst support material, due to their high thermal conductivity, high mechanical strength, low specific weight, and chemical inertness [36].Among all aforementioned good properties, SiC is also a well-known microwave-susceptible material. In this SiC can be heated easily with microwave due to its semiconductivity [37]. As a catalyst support and microwave absorber, two different commercial polytypes of SiC, namely 6H–SiC and 3C-SiC were investigated. Before the mechanical mixing of Ni/Al_2O_3 and SiC polytypes, we first investigated the heating performance of the SiC polytypes alone.

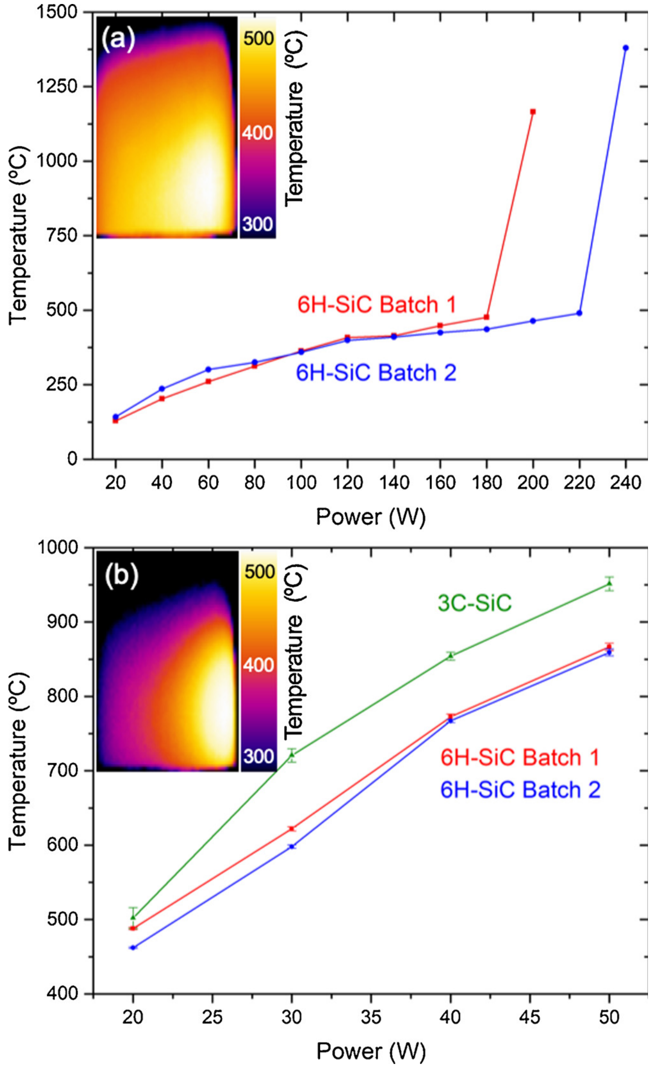

Fig. 4. (a) Heating tests for 6H–SiC and (b) 6H–SiC after runaway and 3C–SiC under 100 mL·min^{-1} of N_2 flow (inset: fixed-bed temperature distribution (a) before the thermal runaway at 140 W and (b) after thermal runaway at 20 W).

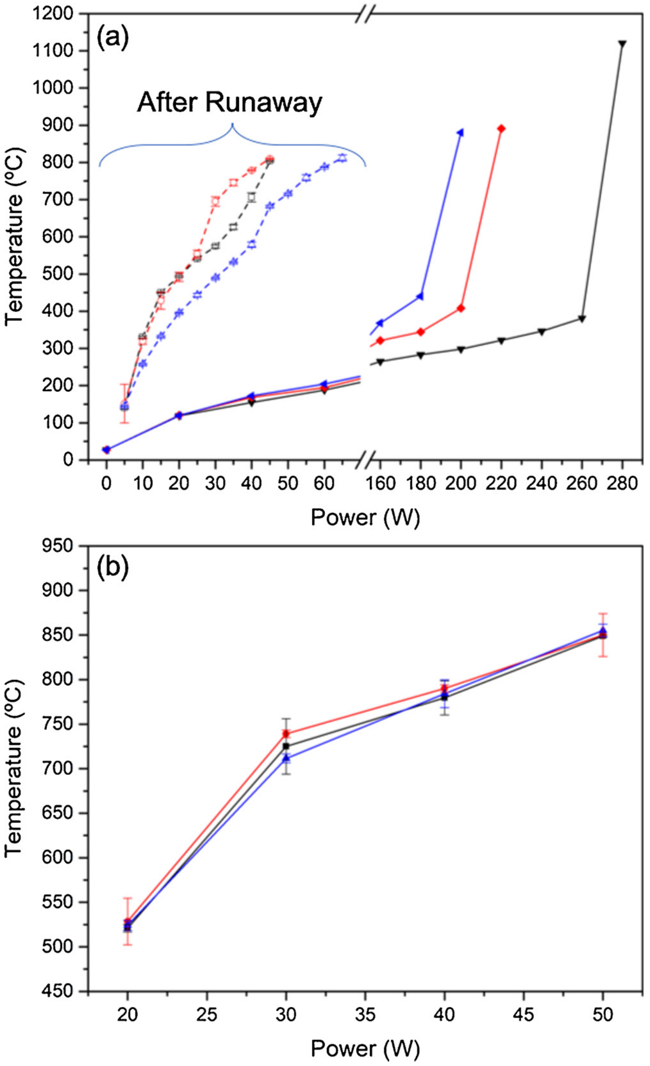

Fig. 5. Temperature profiles of the 50/50 wt% mixture of Ni/Al_2O_3 with (a) 6H–SiC before (solid lines) and after (dotted lines) thermal runaway, and (b) 3C–SiC.

The heating profiles of two different fresh batches of 6H-SiC are presented in Fig. 4. It is clear that 6H-SiC requires high microwave power inputs in order to achieve the desired temperatures. In addition, the continuous microwave heating caused thermal runaways, that were observed approximately at 500 °C for two different batches, see Fig. 4(a). It has been reported that the dielectric loss of SiC at the 2.45 GHz is increased from 1.71 to 27.99 at 20 °C and 695 °C, respectively [37]. This exponential increment in the dielectric loss leads to thermal runaway. When the thermal runaways occurred, microwave generator was immediately stopped to avoid the damage of the quartz reactor tube. After the runaway had occurred and the reactor had been cooled down to room temperature, the same batches of the catalyst were heated up again. Unexpectedly, the microwave power input necessary to reach 500 °C was now reduced by ca. 80%, see Fig. 4(b). The desired temperatures for DRM experiments, *i.e.*, 600, 700 and 800 °C were reached with the microwave power inputs of 40, 60 and 80 W, respectively. Also, the overall fixed-bed temperature distribution changed significantly after the thermal runaway process, see the insets in Fig. 4. The temperature distribution was more homogeneous before the runaway.

Fig. 4(b) depicts the heating profile of 3C-SiC. In this polytype, no thermal runaways were observed during several heating tests. It is clear that 3C-SiC presents a better heating behavior and the temperature reaches up to 950 °C with only a 50 W microwave power input. The above described behavior could be explained with the electron mobility of these different SiC polytypes. Roschke et al. [38] studied and developed the electron mobility models in the three most important silicon carbide polytypes, namely, 4H-, 6H-, and 3C-SiC. Regarding their work, 3C-SiC has higher electron mobility compared with 4H-SiC and 6H-SiC polytypes (650, 950, and 420 cm^2/V/s, respectively) [38]. Apparently, the thermal runaway partially transformed the 6H-SiC polytype into the 4H-SiC and 3C-SiC polytypes (mixture of polytypes), which have more electron mobility than the 6H-type.

After studying the heating performances of SiC polytypes, Ni/Al_2O_3 were mixed mechanically with 6H-SiC and 3C-SiC by 50/50 wt% and subjected to microwave heating for the thermal stability test. The heating results are presented in Fig. 5. The thermal runaway of 6H–SiC was still present even in the mechanical mixture with Ni/Al_2O_3, see Fig. 5(a). After the thermal runaways, the desired temperatures, *i.e.* 700 and 800 °C, were reached with relatively low microwave power inputs in the range of 30 – 65 W, see Fig. 5(b). As mentioned before, this is due to the phase changes of 6H-SiC. Since this phase transformation occurred partially, more thermal runaways were observed in the subsequent heating trials. In the case of mechanical mixture of 3C-SiC and Ni/Al_2O_3, see Fig. 5(b), reproducible heating profiles were obtained in different batches, without any thermal runaways. The desired

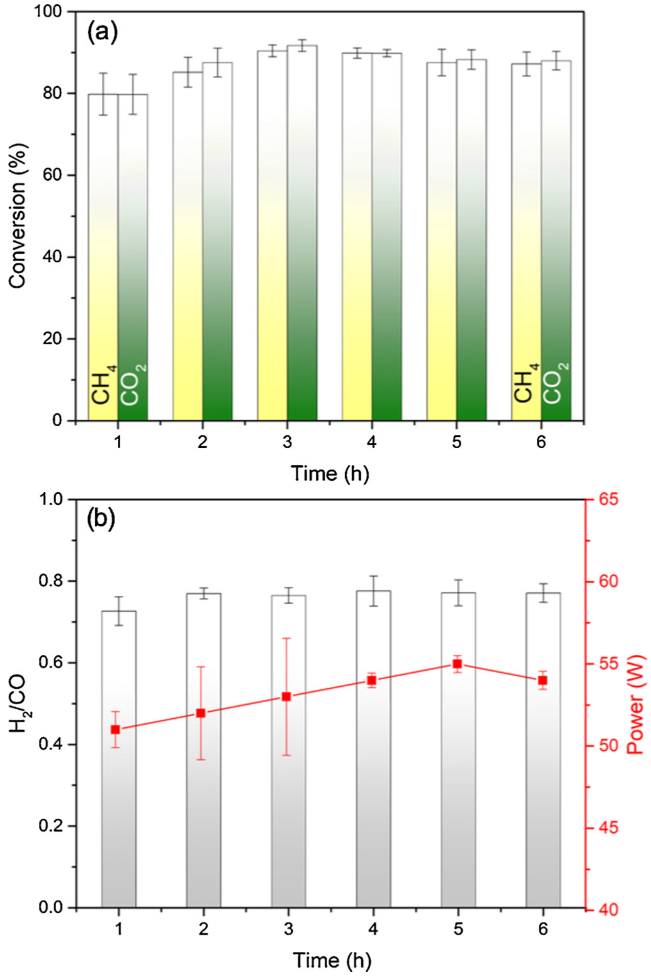

Fig. 6. Catalytic performance of the mechanical mixture of 3C–SiC and Ni/ Al_2O_3 at 800 °C in terms of (a) CH_4 and CO_2 conversions (b) H_2/CO ratios and supplied microwave power inputs.

temperatures of 700 and 800 °C were reached with 30 and 40 W microwave inputs, respectively. The XRD characterization of the mechanical mixture of 3C-SiC and Ni/Al_2O_3 was presented as supplementary information. Due to the temperature instabilities, *i.e.*, thermal runaways, only the mechanical mixture of 3C-SiC and Ni/Al_2O_3 was subjected to the catalytic performance tests.

The conversions of CH_4 and CO_2 at 800 °C, the corresponding H_2/CO ratios, and the supplied microwave power inputs are presented in Fig. 6. During the stability test, the conversions of CH_4 and CO_2 were stable and no catalyst deactivation was observed. After 6 h, the average conversions of CH_4 and CO_2 were ca. 90% at 800 °C and WHSV of 11,000 mL/g/h, see Fig. 6(a). Fidalgo et al. [23] also achieved the same CH_4 conversion at the same temperature but with a lower space velocity (WHSV: 1500 mL/g/h), while using a mechanical mixture of Ni/Al_2O_3 and activated carbon, FY5. However, they achieved higher CO_2 conversion (97%), and they claimed that this was due to the *in situ* carbon gasification (C+ $CO_2 \rightleftharpoons$CO). The thermodynamic calculations at 800 °C resulted in CH_4 and CO_2 conversions of 96.3% and 88.7%, respectively.

The fluctuations in conversions, see Fig. 6, are mainly due to the microwave power fluctuations necessary to maintain the desired temperature. There was also hot-spot formation, which altered the conversions of CH_4 and CO_2. Nevertheless, these results indicate that the mechanical mixture of 3C-SiC and Ni/Al_2O_3 is a good candidate for the DRM process. The same catalyst mixture was also tested under the conventional thermal heating at 800 °C. The tests showed (see the Supplementary information) a fast catalyst deactivation observed during the first hour, and the conversions of CH_4 and CO_2 reaching a value of 79% during the second and third hour. The conventional heating experiment was performed for 3 h only, because the pressure increased inside the reactor reaching 202 kPa, which was the maximum allowable pressure for the experimental set-up. Such behavior was only seen in the conventional heating. It could be attributed to the coke formation when the samples were subjected to the conventional heating.

3.1.4. Nickel on 3C–SiC, Ni/SiC

Even though the mechanical mixture of 3C-SiC and Ni/Al_2O_3 can be used in DRM process, the temperature homogeneity must be improved further. This can be done by removing Al_2O_3 form the mixture, since alumina has relatively low thermal conductivity and poor dielectric properties compared to 3C-SiC. For that reason, we prepared a nickel-impregnated 3C-SiC catalyst and subjected it to the DRM performance tests.

The catalytic performance of Ni/SiC was tested with a CH_4/CO_2 feed ratio of 1 at 700 and 800 °C at a WHSV of 11,000 mL/g/h. Three different batches were prepared and tested at the desired temperatures, in order to ensure the reproducibility of the test. The conversions of CH_4 and CO_2 at different temperatures, the corresponding H_2/CO ratios, and the supplied power inputs are presented in Fig. 7. The XRD characterization of the Ni/SiC was presented as supplementary information.

Compared to the mechanical mixture of 3C-SiC and Ni/Al_2O_3, the same conversions of CH_4 and CO_2 and slightly higher ratios of H_2/CO were observed. In terms of the supplied microwave power inputs (see

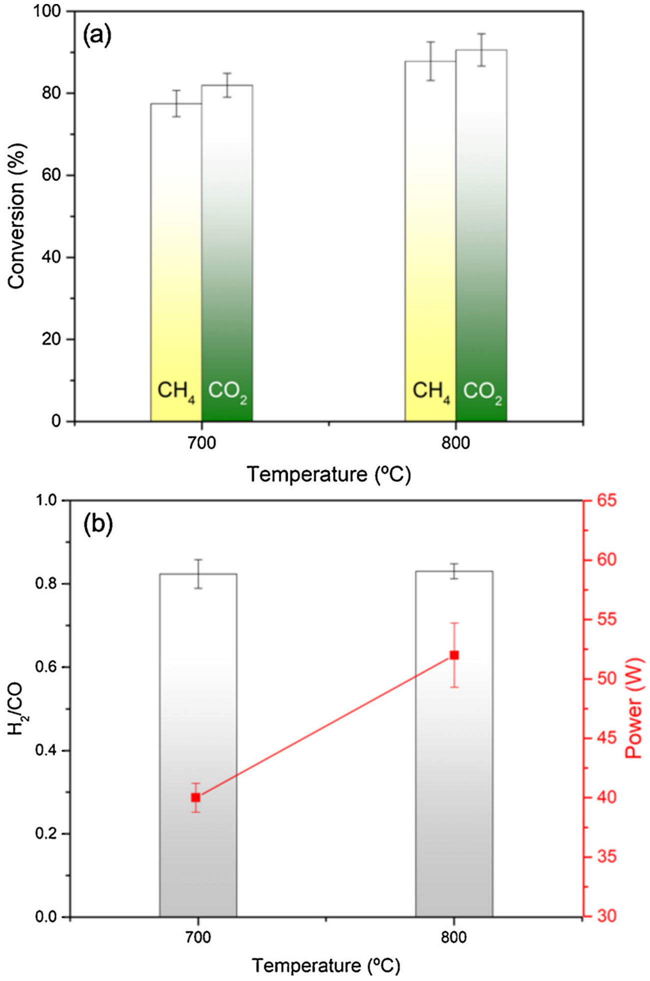

Fig. 7. Catalytic performance of Ni/SiC at 700 and 800 °C in terms of (a) CH_4 and CO_2 conversions (b) H_2/CO ratios and supplied microwave power inputs.

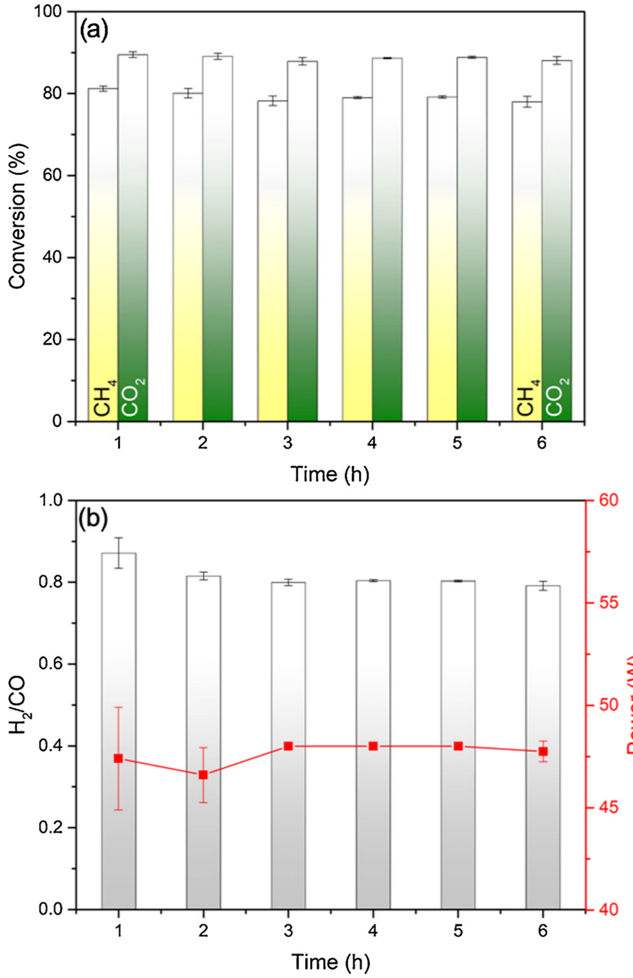

Fig. 8. Catalytic performance of Ni/SiC at 800 °C in terms of (a) CH_4 and CO_2 conversions (b) H_2/CO ratios and supplied microwave power inputs.

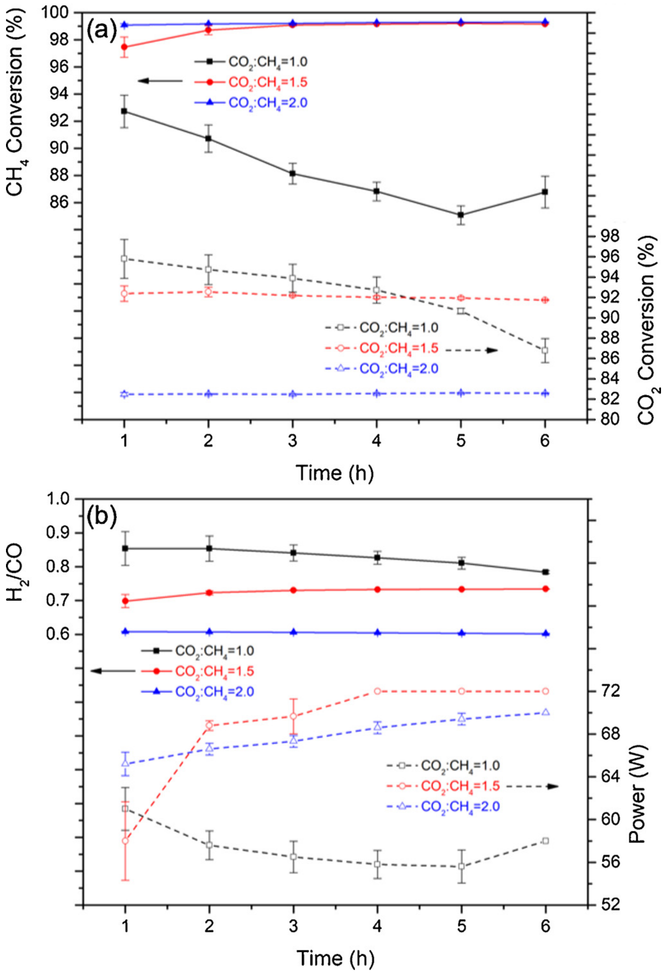

Fig. 9. Influence of the ratios of CO_2:CH_4 in (a) conversions of CH_4 and CO_2 (b) H_2/CO ratios and supplied microwave power inputs.

Fig. 7(b)), the results were similar to the mechanical mixing experiment; however, the fluctuations of the supplied power during the test were lower. Due to the higher conversions obtained, the 6-h stability test was conducted at 800 °C, see Fig. 8. It is clear that the conversion of CO_2 is significantly higher than the conversion of CH_4. This could be explained by the simultaneous carbon gasification with CO_2. These differences in the conversions of CH_4 and CO_2 were less pronounced in the case of the mechanical mixture of 3C-SiC and Ni/Al_2O_3, because the presence of Al_2O_3 delayed the carbon formation.

3.2. Optimization of the operational conditions for Ni/SiC catalyst

As described above, higher conversions and homogenous temperature distribution were obtained with Ni/SiC when compared to Pt/C and the mechanical mixture of Ni/Al_2O_3 and 3C-SiC. For that reason, we continued to study the Ni/SiC catalyst at different feed ratios (CO_2:CH_4) at 800 °C. It is expected that higher feed ratios (CO_2:CH_4) might increase the catalyst stability because CO_2 can not only react with CH_4 but can also react with the carbon formed during the DRM process. The corresponding results of the conversions of CH_4 and CO_2, H_2/CO ratios and the supplied microwave power inputs are presented in Fig. 9.

As expected, the complete conversion of CH_4 was observed at higher ratios of CO_2/CH_4. On the other hand, the conversion of CO_2 (see Fig. 9(a)) was higher at the ratio of 1 but there was a slight decrease in the conversion of CO_2 over time. When the feed ratio of CO_2:CH_4 was increased to 1.5 and 2, the conversion of CO_2 was constant for 6 h. Most of the methane was reacted, that produced a fixed amount of hydrogen, while there was an increase in the amount of CO because of the aforementioned carbon gasification with CO_2. The difference in the H_2/CO ratio for 1.5 and 2 could indicate that in order to maximize the lifetime of the catalyst a ratio of 2 would be beneficial, due to the reduction of the amount of carbon formed during the DRM reaction. In such case, we see higher conversion of CO_2 (> 20%) compared to the work of Xu et al. [34]. (CO_2:CH_4:N_2 = 2:1:0.8, WHSV = 9944 mL/g/h, 11.8 wt% Ni, 101 kPa, 800 °C). Regarding the supplied microwave power input, its increase at higher ratios might be explained by the fact that two endothermic reactions are taking place at the same time, see Fig. 9(b). It can be concluded that the best results in terms of conversions and power consumption over the studied period was obtained with the ratio of 1.5.

To finalize the study of Ni/SiC, it is necessary to analyze the influence of the space velocity and determine the relation between the conversions and the reactants flow. This test was performed at 800 °C for two hours with a feed ratio CO_2/CH_4: 1.5. Due the limitations of the experimental set-up we studied WHSV’s up to 24,000 mL/g/h. The results in terms of the conversion of CH_4 and CO_2 and corresponding microwave power inputs are presented in Fig. 10. A linear decrease in both CH_4 and CO_2 conversion was seen. Despite that decrease, 93% methane and 88% CO_2 conversions at the highest WHSV were observed. As can be seen in Fig. 10, larger WHSVs required slightly higher power in order to keep the temperature constant. This is logical and results from the larger volume treated.

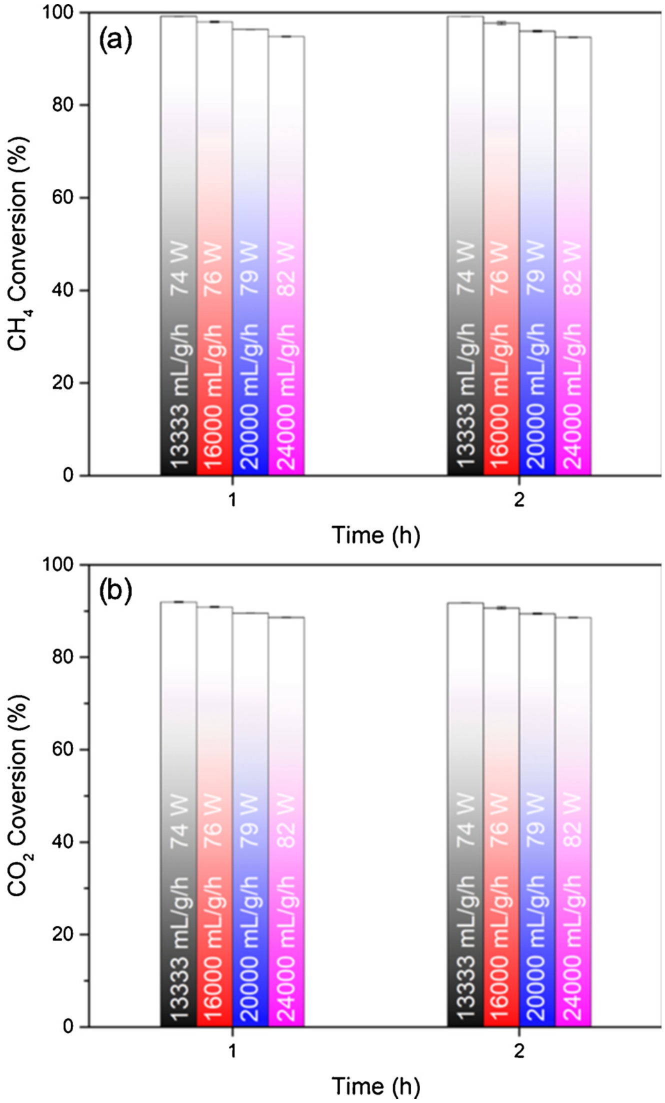

Fig. 10. Influence of the space velocity on the conversion of (a) CH_4 and (b) CO_2.

4. Conclusions

In this work, microwave-assisted dry reforming of methane was carried out in a custom-designed rectangular mono-mode microwave applicator. Several commercial catalyst-supports and their combinations, *i.e.*, Pt/C, Ni/Al_2O_3, mechanical mixture of Ni/Al_2O_3-SiC and Ni/SiC, were studied. Since Ni/Al_2O_3, the most common DRM catalyst, cannot be heated up by microwave, the desired process temperatures were reached after mechanical mixing of the catalyst with 3C-SiC, using a moderate microwave power input (50–55 W). During the stability test of the mechanical mixture of Ni/Al_2O_3-SiC, the conversions of CH_4 and CO_2 were stable and no significant catalyst deactivation was observed, compared to Pt/C catalyst. After 6 h, the average conversions of CH_4 and CO_2 were 90% at 800 °C and WHSV of 11,000 mL/g/h, while the conventional heated catalyst yielded 79% conversion of both CH_4 and CO_2. Furthermore, we demonstrated that nickel-impregnated SiC, Ni/SiC, might be a good, cheap and suitable candidate for the microwave-assisted dry reforming of methane. The short-term stability test showed the CH_4 and CO_2 conversions of 80% and 90%, respectively. Further optimization of the Ni/SiC catalyst and long-term stability tests are needed to arrive at an industry-relevant process concept.

Supporting information

The XRD characterization of the mechanical mixture of 3C-SiC and Ni/Al_2O_3 and Ni/SiC was supplied as supporting information in Figs S1 and S2, respectively. Moreover, the results of DRM reaction of the mechanical mixtures of SiC and Ni/Al_2O_3 under conventional thermal heating presented in Fig. S3.

CRediT authorship contribution statement

Ignacio de Dios García: Investigation, Validation. **Andrzej Stankiewicz:** Writing - review & editing. **Hakan Nigar:** Writing - original draft, Writing - review & editing, Visualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the European Union’s Horizon 2020 Research and Innovation Programme (ADREM project – Grant Agreement No. 680777).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.04.045.

References

[1] F.A. Rahman, M.M.A. Aziz, R. Saidur, W.A.W.A. Bakar, M.R. Hainin, R. Putrajaya, N.A. Hassan, Pollution to solution: capture and sequestration of carbon dioxide (CO2) and its utilization as a renewable energy source for a sustainable future, Renew. Sustain. Energy Rev. 71 (2017) 112–126.
[2] Earth System Research Laboratory, Global Monitoring Division, (2019) (Accessed 01 November 2019), https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html.
[3] G. Zhang, J. Liu, Y. Xu, Y. Sun, A review of CH4–CO2 reforming to synthesis gas over Ni-based catalysts in recent years (2010–2017), Int. J. Hydrogen Energy 43 (2018) 15030–15054.
[4] D. Pakhare, J. Spivey, A review of dry (CO2) reforming of methane over noble metal catalysts, Chem. Soc. Rev. 43 (2014) 7813–7837.
[5] T.S. Phan, A.R. Sane, B. Rêgo de Vasconcelos, A. Nzihou, P. Sharrock, D. Grouset, D. Pham Minh, Hydroxyapatite supported bimetallic cobalt and nickel catalysts for syngas production from dry reforming of methane, Appl. Catal. B 224 (2018) 310–321.
[6] O. Daoura, M.N. Kaydouh, N. El-Hassan, P. Massiani, F. Launay, M. Boutros, Mesocellular silica foam-based Ni catalysts for dry reforming of CH4 (by CO2), J. Co2 Util. 24 (2018) 112–119.
[7] M.K. Nikoo, N.A.S. Amin, Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation, Fuel Process. Technol. 92 (2011) 678–691.
[8] B. Nematollahi, M. Rezaei, M. Khajenoori, Combined dry reforming and partial oxidation of methane to synthesis gas on noble metal catalysts, Int. J. Hydrogen Energy 36 (2011) 2969–2978.
[9] Z. Liu, P. Lustemberg, R.A. Gutiérrez, J.J. Carey, R.M. Palomino, M. Vorokhta, D.C. Grinter, P.J. Ramírez, V. Matolín, M. Nolan, M.V. Ganduglia-Pirovano, S.D. Senanayake, J.A. Rodriguez, In situ investigation of methane dry reforming on metal/Ceria(111) surfaces: metal–support interactions and C − H bond activation at low temperature, Angew. Chem. – Int. Ed. 56 (2017) 13041–13046.
[10] S. Hamzehlouia, S.A. Jaffer, J. Chaouki, Microwave heating-assisted catalytic dry reforming of methane to syngas, Sci. Rep. 8 (2018).
[11] H.O. Seo, Recent scientific progress on developing supported Ni catalysts for dry (CO2) reforming of methane, Catalysts 8 (2018).
[12] A. Ramirez, J.L. Hueso, M. Abian, M.U. Alzueta, R. Mallada, J. Santamaria, Escaping undesired gas-phase chemistry: microwave-driven selectivity enhancement in heterogeneous catalytic reactors, Sci. Adv. 5 (2019).
[13] H. Nigar, R. Mallada, B. Garcia-Baños, J.M. Catala-Civera, F. Peñaranda-Foix, J. Santamaría, Amine functionalized mesoporous silica for selective microwave heating, AMPERE 2015 – 15th International Conference on Microwave and High Frequency Heating (2015) 40.
[14] X. Wang, M. Fan, X. Huang, M. Tang, G. Yu, H. Liu, F. Wang, H. Adidharma, K.A.M. Gasem, M. Radosz, High-performance nano-structured Ni based catalysts for

high-temperature CO2[sbnd]CH4 reforming—greenhouse gases to syngas, Catal. Today 339 (2020) 344–351.

[15] L.A. Arkatova, N.G. Kasatsky, Y.M. Maximov, O.V. Pakhnutov, A.N. Shmakov, Intermetallides as the catalysts for carbon dioxide reforming of methane, Catal. Today 299 (2018) 303–316.

[16] Q. Ma, L. Guo, Y. Fang, H. Li, J. Zhang, T.S. Zhao, G. Yang, Y. Yoneyama, N. Tsubaki, Combined methane dry reforming and methane partial oxidization for syngas production over high dispersion Ni based mesoporous catalyst, Fuel Process. Technol. 188 (2019) 98–104.

[17] Q. Wei, G. Yang, Y. Yoneyama, T. Vitidsant, N. Tsubaki, Designing a novel Ni-Al2O3-SiC catalyst with a stereo structure for the combined methane conversion process to effectively produce syngas, Catal. Today 265 (2016) 36–44.

[18] A. Stankiewicz, F.E. Sarabi, A. Baubaid, P. Yan, H. Nigar, Perspectives of microwaves-enhanced heterogeneous catalytic gas-phase processes in flow systems, Chem. Rec. 19 (2019) 40–50.

[19] S. Horikoshi, N. Serpone, Microwaves in Catalysis: Methodology and Applications, Wiley, 2015.

[20] S. Horikoshi, N. Serpone, Role of microwaves in heterogeneous catalytic systems, Catal. Sci. Technol. 4 (2014) 1197–1210.

[21] B. Fidalgo, A. Domínguez, J.J. Pis, J.A. Menéndez, Microwave-assisted dry reforming of methane, Int. J. Hydrogen Energy 33 (2008) 4337–4344.

[22] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Process. Technol. 91 (2010) 1–8.

[23] B. Fidalgo, A. Arenillas, J.A. Menéndez, Mixtures of carbon and Ni/Al2O3 as catalysts for the microwave-assisted CO2 reforming of CH4, Fuel Process. Technol. 92 (2011) 1531–1536.

[24] B. Fidalgo, J.A. Menéndez, Study of energy consumption in a laboratory pilot plant for the microwave-assisted CO 2 reforming of CH 4, Fuel Process. Technol. 95 (2012) 55–61.

[25] L.S. Gangurde, G.S.J. Sturm, M.J. Valero-Romero, R. Mallada, J. Santamaria, A.I. Stankiewicz, G.D. Stefanidis, Synthesis, characterization, and application of ruthenium-doped SrTiO3 perovskite catalysts for microwave-assisted methane dry reforming, Chem. Eng. Process. – Process Intensif. 127 (2018) 178–190.

[26] L. Gangurde, Process Intensification of Microwave Assisted Methane Dry Reforming, Delft University of Technology, 2018.

[27] L.S. Gangurde, G.S.J. Sturm, T.J. Devadiga, A.I. Stankiewicz, G.D. Stefanidis, Complexity and challenges in noncontact high temperature measurements in microwave-assisted catalytic reactors, Ind. Eng. Chem. Res. 56 (2017) 13379–13391.

[28] H. Nigar, B. Garcia-Baños, F.L. Peñaranda-Foix, J.M. Catalá-Civera, R. Mallada, J. Santamaría, Amine-functionalized mesoporous silica: a material capable of CO2 adsorption and fast regeneration by microwave heating, AlChE J. 62 (2016) 547–555.

[29] H. Nigar, I. Julián, R. Mallada, J. Santamaría, Microwave-assisted catalytic combustion for the efficient continuous cleaning of VOC–containing air streams, Environ. Sci. Technol. 52 (2018) 5892–5901.

[30] H. Nigar, G.S.J. Sturm, B. Garcia-Baños, F.L. Peñaranda-Foix, J.M. Catalá-Civera, R. Mallada, A. Stankiewicz, J. Santamaría, Numerical analysis of microwave heating cavity: combining electromagnetic energy, heat transfer and fluid dynamics for a NaY zeolite fixed-bed, Appl. Therm. Eng. 155 (2019) 226–238.

[31] S. Wang, G.Q. Lu, G.J. Millar, Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: state of the art, Energy Fuels 10 (1996) 896–904.

[32] W.J. Jang, J.O. Shim, H.M. Kim, S.Y. Yoo, H.S. Roh, A review on dry reforming of methane in aspect of catalytic properties, Catal. Today 324 (2019) 15–26.

[33] N.A.K. Aramouni, J.G. Touma, B.A. Tarboush, J. Zeaiter, M.N. Ahmad, Catalyst design for dry reforming of methane: analysis review, Renew. Sustain. Energy Rev. 82 (2018) 2570–2585.

[34] Z. Xu, Y. Li, J. Zhang, L. Chang, R. Zhou, Z. Duan, Bound-state Ni species – a superior form in Ni-based catalyst for CH4/CO2 reforming, Appl. Catal. A Gen. 210 (2001) 45–53.

[35] M.K. Park, H.N. Kim, S.S. Baek, E.S. Kang, Y.K. Baek, D.K. Kim, Dielectric properties of alumina ceramics in the microwave frequency at high temperature, IUMRS International Conference in Asia 2006, IUMRS-ICA 2006, Trans Tech Publications Ltd, Jeju, 2007, pp. 743–746.

[36] H. Abderrazak, E.s. Hmida, Silicon Carbide: Synthesis and Properties, (2011).

[37] R. Gerhardt, Properties and Applications of Silicon Carbide, IntechOpen, 2011.

[38] M. Roschke, F. Schwierz, Electron mobility models for 4H, 6H, and 3C SiC, IEEE Trans. Electron Devices 48 (2001) 1442–1447.