REACTION ENGINEERING, KINETICS AND CATALYSIS

Electrified methane steam reforming on a washcoated SiSiC foam for low-carbon hydrogen production

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Funding information
H2020 European Research Council, Grant/Award Number: 694910

Abstract

In view of largely available renewable electricity as a green future resource, here we report the electrification of a Rh/Al_2O_3 washcoated SiSiC foam for methane steam reforming (MSR). We show that, thanks to the suitable bulk resistivity of the SiSiC foam, its direct Joule heating up to relevant temperatures is feasible; the interconnected geometry greatly reduces heat and mass transfer limitations, which results in a highly active and energy efficient system for low-carbon H_2 production. The foam-based electrified MSR (eMSR) system showed almost full methane conversion above 700°C and methane conversions approaching equilibrium were obtained in a range of conditions. Energy efficiency as high as 61% and specific power consumption as low as 2.0 $kWh/Nm^3_{H_2}$ were measured at 650°C, at gas hourly space velocity (GHSV) of 150,000 $cm^3/h/g_{cat}$. When driven by renewable electricity, the proposed reactor configuration promises a high potential to address the decarbonization challenge in the near-term future.

KEYWORDS
direct Joule heating, electrification, hydrogen production, methane steam reforming, Rh/Al_2O_3, SiSiC foam

1 | INTRODUCTION

The hydrogen-based energy system, as an efficient and clean approach for delivering high-quality energy services, is widely regarded as a promising option toward a sustainable future.[1] Methane steam reforming (MSR) currently accounts for more than half of the global hydrogen production. Due to its highly endothermic nature, industrial scale MSR is typically carried out in multitubular reactors operated at high flow rates and externally heated by burning an additional amount of methane, which is responsible for roughly half of the CO_2 emission of the process.[1-4] Besides, relatively high dilution makes the recovery of CO_2 from the flue gas more difficult and

expensive than from the main process stream, thus negatively affecting the economics of "blue hydrogen" production. With renewable electricity becoming more and more accessible, the so-called power-to-X (P2X) concept, which presumes the production of energy vectors and chemicals via renewable electricity, represents a promising way to address the challenge of decarbonization.[5-7] On the other hand, such technologies, which can store energy in the form of chemical commodities, offer a solution to manage the fluctuating nature of renewable energy sources, such as wind and solar, thanks to the design of load-following technologies.[8]

Electricity can be converted into heat and transferred to thermally driven chemical reactors in several ways, such as microwave heating,

induction heating as well as Joule heating (also known as Ohmic heating or resistance heating): all these methods have been recently studied to replace the fossil fuel combustion in several industrial processes for chemical syntheses.[5] Reduction of temperature gradients inside the chemical reactors, faster temperature response as well as higher temperatures can be achieved by electric heating in comparison to conventional heating methods, which makes it advantageous against thermodynamic, kinetic, and operational constraints.[9] In this regards, few studies have been reported concerning the electrification of methane reforming.[10–16] Recently, an innovative reactor concept with an electrically heated washcoated FeCrAl-alloy tube ($d_t = 6$ mm) was proposed by Wismann et al.[13–15] They report the experimental and numerical investigation of a system based on a steel tube connected to a power generator with an internal coating of Ni-based catalysts. The system was operated in such a way that outlet temperature up to 900°C and methane conversion close to 87% were obtained. As environmental benefit, a CO_2 reduction of 20%–50% was reported when compared with industrial reformers, with a computed thermal efficiency around 70% and a power density of about 10 MW/m^3. Similar approaches were reported by Renda et al.[10] and Rieks et al.[11] for methane reforming. In these studies, commercial heating elements (silicon carbide or FeCrAl alloy) were coated with a thin layer of Ni-based catalysts and loaded in tubular reactors. Such approach is promising to realize an efficient heat transfer from the resistance to the catalyst. The systems were able to reach temperature levels in excess of 700°C. Renda et al.[10] reported the conversions close to thermodynamic equilibrium whereas Rieks et al.[11] reported significantly lower conversions. However, the geometry of the heating elements was not optimized for the catalytic processes. For instance, by-pass phenomena were reported by Rieks et al.[11]

The application of thermally conductive open-cell foams has been studied in our group for strongly endothermic and exothermic catalytic processes.[9,17,18] In particular, our results showed the capability of highly conductive internals to improve the radial heat transfer in MSR, thus minimizing the temperature gradients across the catalytic bed and enhancing the productivity of the system.[19–21] Foam-based substrates can be also regarded as heating resistances for the electrification of catalytic processes since these structures provide a continuity of the solid matrix and therefore enable to apply an electric field across the catalyst support.[22–24] Recently, Dou et al.[22,23] reported the direct electrification of a Ni-Al catalyst-coated Ni foam for CO_2 methanation reaction; herein, a foam temperature of 300°C was reported with an input power of 10 W, which allowed a fast-heating of the reactor during transient operations. In another study, Badakhs et al.[24] investigated the endothermic ammonia cracking reaction by using a NiCrAl foam as catalyst support as well as Joule-heated substrate to supply the reaction thermal duty. With a small reactor volume of 7.7 cm^3, an energy efficiency of ~30% was achieved.

The porous structure of foams enables a higher catalyst inventory compared to conventional tubular or plate-type heating elements thanks to the higher specific surface area. Moreover, they provide high volumetric heat and mass transfer coefficients.[19] Therefore, the application of foams has the potential to overcome heat and mass transfer limitations in electrified methane steam reforming (eMSR), being the external mass transfer one of the limiting factors in the configuration showed by Wismann and coworkers.[13] In this regards, a preliminar numerical study of structured catalyst geometry for electrically heated MSR process has been reported recently by our group,[25] and the results show that it is possible to run the process at unprecedented space velocities thanks to the right combination of foams and a highly active catalyst.

In this study, a novel reactor configuration is proposed and experimentally demonstrated for the electrification of MSR using direct Joule heating of a washcoated foam catalyst. A cylindrical Si-infiltrated silicon carbide foam was washcoated with Rh/Al_2O_3 catalyst and electrically connected to power supply. Thus, it provided optimal heat and mass transfer properties and efficient inner heating for the steam reforming reaction.

2 | EXPERIMENTAL

2.1 | Foam characterization and catalyst preparation

A commercial Si-infiltrated silicon carbide open-cell foam (Erbicol, CH) with cylindrical geometry ($d_{foam} = 3.2$ cm, $L_{foam} = 9.9$ cm, total volume $V_{foam} = 79.6$ cm^3) was adopted in the present work as structured catalyst substrate. The foam geometry was characterized by optical microscopy (a SteREO Discovery V12 instrument equipped with an Axiocam ERc 5 s camera by Zeiss®). The cell diameter (d_{cell}) and the strut diameter (d_s) were obtained by averaging more than 25 measurements from the obtained optical images using an open-source software (ImageJ2x). The total porosity of the foam was estimated by ethanol picnometry.[26] X-ray diffraction (XRD) pattern of the SiSiC foam was recorded using a Bruker Advance D8 diffractometer in a range of $2\theta = 20°–70°$, a step size of 0.05° and a step time of 12.5 s.

The 1%Rh/Al_2O_3 catalyst applied in the present study was prepared by using γ-Al_2O_3 powder (Sasol, PURALOX) as morphological support. An incipient-wet impregnation method was used: at this scope, the pore volume of Al_2O_3 powder was first evaluated by water filling and amounted to 0.8 mL/g. The rhodium precursor (rhodium [III] nitrate solution, Rh 10%–15% w/w, Alfa Aesar) was diluted in deionized water, with water excess of 25% of the total pore volume to ensure homogeneity. The quantity of Rh precursor was properly chosen to meet the specification in the final Rh content with respect to alumina mass (1% w/w). In a next step, the obtained solution was mixed with the fine γ-Al_2O_3 powder, afterward, the obtained sample was dried in oven at 120°C overnight.

The catalyst slurry was prepared before the washcoating process according to the procedures described in the literature.[19,27,28] First, polyvinyl alcohol (PVA, Sigma-Aldrich) was dissolved (0.08:1 w/w with respect to the powder mass) in deionized water (1.8:1 w/w with respect to the powder mass) by exploiting a magnetic stirring at 85°C for 15 minutes. In a next step, glycerol (Sigma-Aldrich) was added (1.9:1 w/w with respect to the powder mass) to the solution, and the

mixture was again stirred until a homogeneous solution was obtained. The solution was then mixed with catalyst powders and ball-milled for 24 h at constant speed (50 rpm) to ensure the powder dispersion in the slurry. Afterward, a small amount of ethanol was added to defoam the slurry.

The washcoating of the SiSiC foam was obtained by dipping the sample in the slurry, spinning (1000 rpm for 10 s) it to remove the excess material and flash drying in oven at 350°C for 5 min. The coating procedure steps were repeated several times till the desired mass of loaded catalyst was reached. Before any catalytic test, the washcoated foam was first loaded in the reactor and subjected to a conditioning treatment at 500°C for 4 h in flowing N_2, with the help of the external heating socket with a ramp of 10°C/min. Considering that the gas feed enters in the reactor with temperature lower than 200°C, which is not sufficient to activate the catalytic reaction, only 3/5 of the foam was washcoated with catalyst. With the proposed solution, the gas can be preheated in the first portion and then react in the second washcoated part.

2.2 | Catalytic activity tests

As shown in Figure 1, the SiSiC foam, washcoated with 1% Rh/Al$_2$O$_3$ catalyst, was placed in a tubular stainless-steel reactor (outer diameter = 5 cm) for the eMSR reaction. A ceramic tube (dense alumina) with a thickness of 5 mm is inserted between the stainless-steel tube and the foam to avoid electric contact. To connect the foam with the power generator, home-made electric contactors were adopted; the electric wires are connected to ¼ inch stainless-steel tubes that are brazed to a steel plate, with four holes for the water and methane feeding. A thin layer of copper foam (Alantum, pore size 800 μm, 1 mm thickness) is placed between the foam and the electrical plate to ensure a good electrical contact. The electrical plates are connected to a power generator (STAMOS, S-LS-76, V_{max} = 30 V, I_{max} = 50 A), which applies a DC current to the system. K-type thermocouples are placed inside the electric contactors to measure the temperatures at the upper side and bottom of the foam. To avoid electric contact, ceramic tubes (dense alumina, d_{out} = 3 mm, d_{in} = 2 mm) are used as thermocouple wells. To avoid any high-temperature bypass originated by the different thermal expansion of materials, a thin layer of Cu foil (0.25 mm thickness) was inserted between the ceramic tube and the stainless-steel tube. Moreover, a layer of quartz tape was placed between the SiSiC foam and the ceramic tube to avoid bypass between the foam and the alumina tube.

Catalytic tests were performed at two different gas hourly space velocities: gas hourly space velocity (GHSV) = 100,000 and 150,000 cm³/h/g$_{cat}$ with a nondiluted gas feed of CH$_4$ and H$_2$O (steam to carbon ratio [S/C] = 4.1:1) at ambient pressure. Downstream from the reactor, water was removed from the products by a condenser and the dry gas mixture was analyzed using an online micro-GC (Agilent, 900 Micro GC). To enable the use of internal standard, an inert gas (nitrogen) was directly fed to the analysis section through a by-pass line (without passing through reactor).
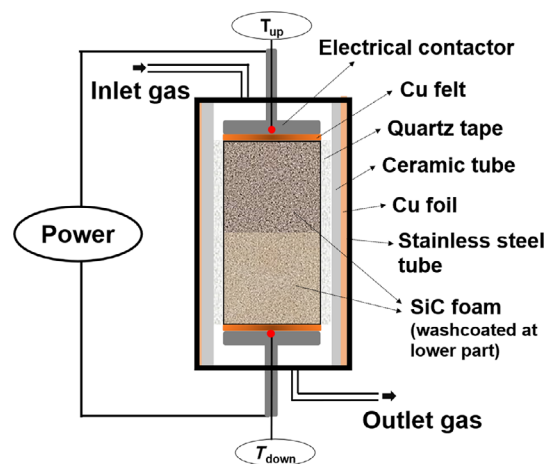
FIGURE 1 Schematic representation of the electrified methane steam reforming reactor layout (T_{up} and T_{down} indicate where temperatures are measured)

Optimal analytical conditions were obtained by setting the nitrogen flowrate at 1/3 of the methane flowrate. Nitrogen and methane were fed to the system by means of mass flow controllers (Brooks), while water was fed with a dosing-evaporation system (Brooks). In a typical experiment, the system was preheated in nitrogen up to 500°C, then water was fed to the system; afterward, the flow of nitrogen was switched to methane to initiate the MSR reaction. We monitored the carbon balance and it was very close to 100% during all the eMSR tests.

2.3 | Data analysis

For each catalytic test, the input voltage (V) and current (I) were recorded from the power generator (STAMOS, S-LS-76). Therefore, the input power (P) and the resistance (R) of the electrical circuit were calculated according to

$$P = VI \tag{1}$$

$$R = \frac{V}{I} \tag{2}$$

The electric resistivity (ρ) of the material was calculated according to

$$\rho = R \cdot \frac{A(1-\varepsilon)F}{l}, \tag{3}$$

where A is the cross-section area of the foam, ε is the porosity of the foam, l is the total length of the foam, and F is a shape-factor that takes in account the geometry of the foam. Based on the analogy between current and heat transport, the correlation proposed by Bracconi et al.[29] for the effective thermal conductivity of open-cell was used to evaluate the shape factor F:

$$F = \left(\frac{1}{3} + \frac{2}{3}(1 - \varepsilon)\right) \qquad (4)$$

Methane conversion (X_{CH_4}) was calculated according to

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}, \qquad (5)$$

where $F_{CH_4,in}$ and $F_{CH_4,out}$ are the methane flow rates in the feed and in the product stream, respectively. Equilibrium conversion at given temperature, pressure, and feed composition was obtained using linearized expressions for the Gibbs free energies for the MSR and water gas shift reaction (WGS).[30]

To evaluate the process heat duty, the power loss and the energy efficiency of the proposed eMSR system, the input and output enthalpy flows were evaluated under the hypothesis of ideal mixture and perfect gas according to the following relation:

$$\dot{H} = \sum \dot{n}_i \cdot h_i(T) = \sum \dot{n}_i \cdot \left(\Delta h_{F,i}^{\circ}(T_{ref}) + \int_{T_{ref}}^{T} C_{P,i}(T)dt\right), \qquad (6)$$

where $\dot{n}_i$ is the molar flow rate, $h_i(T)$ is the enthalpy, T_{ref} is the reference temperature (296.15 K), $\Delta h_{F,i}^{\circ}(T_{ref})$ is the enthalpy of formation at T_{ref} and $C_{P,i}$ is the specific heat capacity.[30] In this regard, the process heat duty (Q) was calculated according to the following equation:

$$Q = \dot{H}_{out} - \dot{H}_{in}, \qquad (7)$$

where $\dot{H}_{in}$ and $\dot{H}_{out}$ are the enthalpy flows of the gas mixtures at inlet and outlet of the reactor, respectively. In this regard, the power loss (P_{loss}) as well as the energy efficiency (η) of the system can be calculated according to Equations 8 and 9, respectively:

$$P_{loss} = P - Q \qquad (8)$$

$$\eta = \frac{Q}{P} \qquad (9)$$

The power density of the system was calculated based on the total volume of the foam ($V_{foam} = 79.6$ cm^3) according the following equation:

$$\text{Power density} = \frac{P}{V_{foam}} \qquad (10)$$

The specific power consumption per unit of hydrogen production, in unit of kWh/Nm$^3_{H_2}$, is calculated based on the input power (P) and the produced H$_2$ flow rate ($F_{H2,out}$) by the following equation:

$$\text{Power consumption} = \frac{P}{F_{H_2,out}} \qquad (11)$$

Finally, the hydrogen productivity was calculated based on the produced H$_2$ flow rate ($F_{H2,out}$) and the applied catalyst amount (m_{cat}) according to the following equation:

$$\text{Hydrogen productivity} = \frac{F_{H_2},out}{m_{cat}} \qquad (12)$$

3 | RESULTS AND DISCUSSION

3.1 | SiSiC foam and washcoating

The geometrical and phase composition properties of the SiSiC foam adopted in this study are summarized in Table 1. The cell diameter (d_{cell}), that is, the diameter of the single repeated unit that constitutes the foam, as well as the strut diameter (d_{strut}), that is, the characteristic transversal length of the solid ligaments, were measured by optical microscopy.[31,32] The total porosity of 0.88 was estimated by ethanol picnometry.[26] A surface to volume ratio (Sv) of 740 m^{-1} was calculated using the model developed by Ambrosetti et al.[32] Figure 2 presents the XRD pattern of the foam. The result shows the presence of both SiC (PDF#49–1428) and Si phase (PDF#75–0589).[33]
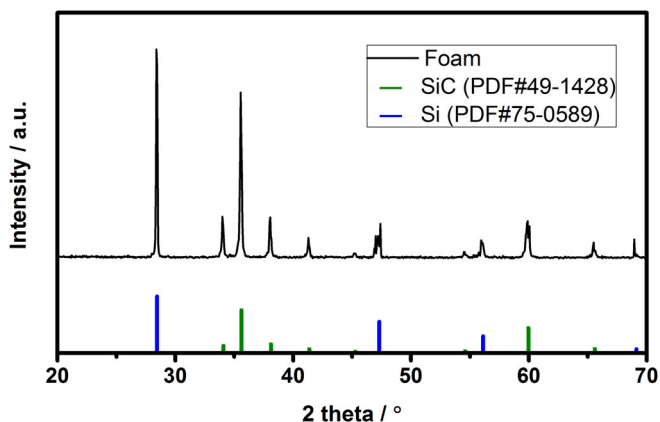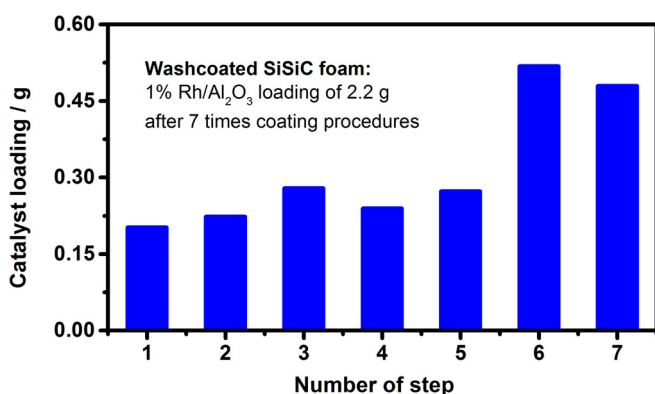
The results of catalyst loading per deposition step during the washcoating process are shown in Figure 3. The final catalyst loading on the foam was 2.2 g after seven repeated coating steps. This loading corresponds to 46 g/L considering that only 3/5 of the foam volume was used for washcoating. By assuming a coating density of 1.3 g/cm^3, we evaluated a coating thickness of 45 μm, a value that ensure a very limited impact of internal mass transfer limitations. Figure 4 shows the obtained catalyst washcoated SiSiC foam applied in this study. A good and homogeneous coverage of the catalyst on the foam surface was achieved, as shown in Figure 4C, without any relevant pore clogging phenomena.
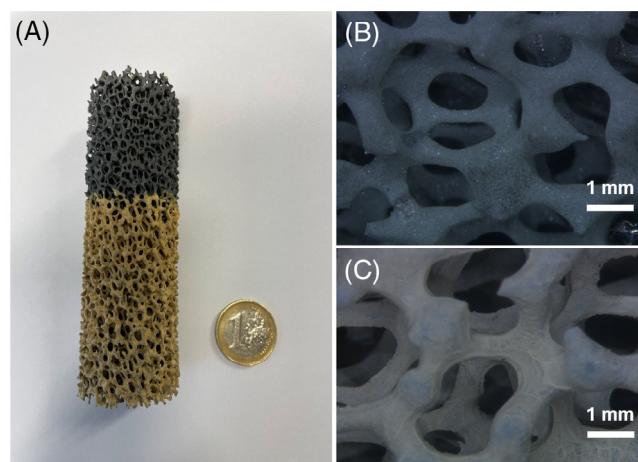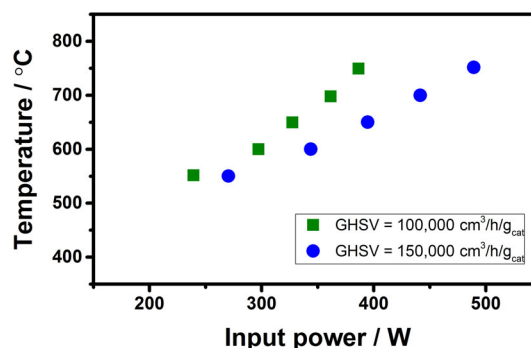
3.2 | Catalytic and energy performances

Two series of experiments were carried out with GHSV of 100,000 and 150,000 cm^3/h/g$_{cat}$ at ambient pressure. For each space velocity, the catalytic performances were evaluated at various downstream temperatures (T_{down}, as shown in Figure 1), which were achieved by manipulating the input electric voltage. The resulting current output was measured to estimate the resistance. As shown in Figure 5, an approximately linear correlation was noticed between the measured T_{down} temperature and the corresponding input power. From voltage/current measurements, an almost constant electrical resistance of the system was calculated (0.41–0.45 Ω), as reported in Table 2. The small increase of the electrical resistance with growing temperature is consistent with a previous study where a small positive temperature coefficient of resistance was reported for commercial SiC elements above

TABLE 1 Geometrical and phase properties of the foam applied in this study

d_{cell} (mm)	d_{strut} (mm)	Porosity (%)	Surface to volume ratio (m^{-1})	Phase composition
3.32	0.61	88	740	SiC/Si

FIGURE 2 X-ray diffraction pattern of the SiSiC foam recorded using a Bruker Advance D8 diffractometer in a range of $2\theta = 20°–70°$, a step size of $0.0150°$ and a time step of 12.5 s

FIGURE 3 Catalyst loading per deposition step during the washcoating process

FIGURE 4 Washcoated foam: (A) the Rh/Al$_2$O$_3$ catalyst washcoated SiSiC foam investigated in this study; (B) optical microscopy image from the bare part of the foam; (C) optical microscopy image from the washcoated part of the foam

FIGURE 5 Measured T_{down} temperature as a function of input power during the eMSR runs. Experimental conditions: 1% Rh/Al$_2$O$_3$ washcoated on SiSiC foam with a catalyst loading of 2.2 g, feed mixture of CH$_4$ and H$_2$O with steam to carbon ratio (S/C) of 4.1:1, GHSV of 100,000 (green squares) and 150,000 cm^3/h/g$_{cat}$ (blue circles). eMSR, electrified methane steam reforming; GHSV, gas hourly space velocity

600°C.[34] Moreover, the electrical resistivity obtained by Equation 3 was around 0.012 Ω·cm, which is in the range of the values reported for commercial SiC elements in the investigated temperature range.[34] This indicates that the proposed eMSR system works without major effects of contact resistance. Moreover, as a result of the suitable bulk electrical resistivity of the employed SiSiC material, moderate voltages and currents are observed (Table 2), in line with our preliminary numerical study.[25] In contrast, metallic materials such as FeCrAlloy[13] exhibit lower resistivities, so that for the foam geometry herein investigated too high currents (and very low voltages) are needed for the same power required by the reactor, leading to an increase of power losses. Another advantage of the SiSiC material over FeCrAlloy is its higher thermal conductivity,[35] which is favorable for a more uniform temperature distribution. The lower slope of the heating curve at the high space velocity condition (Figure 5) is consistent with the higher heat duty of the reactor at fixed outlet temperature according to

Equation 7. Apart from the electric heating, thanks to its tortuous flow path the open-cell foam structure could reduce the external mass transport limitations compared to laminar flow in a wall-coated reactor or in coated monolith channels, which can further contribute to the intensification of the eMSR. This has been evidenced by our previous numerical simulation results.[25]

Before the MSR tests over the washcoated foam, blank experiments were carried out over the empty foam, that is, without the catalytic washcoat. Hardly any methane conversion was noticed when the directly electrified bare SiSiC foam was exposed to the methane

TABLE 2 Summary of results from electrified methane steam reforming runs

GHSV (cm³/h/g_cat)	Voltage (V)	Current (A)	Input power, P (W)	T_down (°C)	Resistance, R [Ω]	Enthalpy duty, Q [W]	Power density (MW/m³)	Power consumption (kWh/Nm³_H₂)
100,000	12.67	30.75	386.4	749	0.41	181	4.86	2.91
	12.30	29.40	361.6	698	0.42	173	4.54	2.66
	11.90	27.52	327.5	650	0.43	165	4.11	2.43
	11.37	26.15	297.2	600	0.43	149	3.74	2.36
	10.25	23.33	239.1	552	0.44	120	3.01	2.52
150,000	14.10	34.70	489.3	752	0.41	274	6.15	2.34
	13.60	32.47	441.6	700	0.42	261	5.55	2.13
	13.04	30.26	394.6	650	0.43	240	4.96	2.00
	12.25	28.07	343.8	600	0.44	202	4.32	2.10
	11.00	24.58	270.4	550	0.45	164	3.40	2.29

Abbreviation: GHSV = gas hourly space velocity.
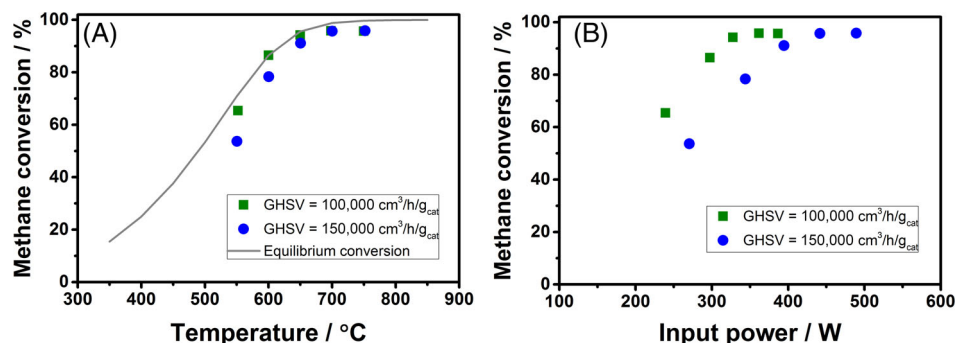
FIGURE 6 Results from electrified methane steam reforming runs: (A) measured methane conversion as a function of measured T_{down} temperature; (B) measured methane conversion as a function of input power. Experimental conditions: 1% Rh/Al_2O_3 washcoated on SiSiC foam with a catalyst loading of 2.2 g, feed mixture of CH_4 and H_2O with steam to carbon ratio (S/C) of 4.1:1, GHSV of 100,000 (green squares) and 150,000 cm³/h/g_cat (blue circles). GHSV, gas hourly space velocity

TABLE 3 Comparison of the results of this study with previous studies

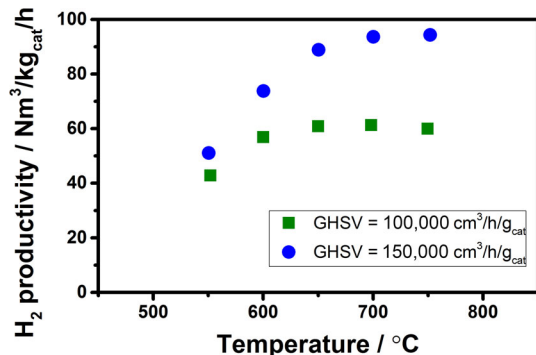| No.	Reactor configuration	Feed condition	Catalytic performance	Ref.
1	Electrification of FeCrAl-alloy tube washcoated with Ni-based catalyst	$CH_4/H_2O/H_2$ = 30/60/10; 50 mbar, 102 L/h	X_{CH_4} = 87% at 700°C	13
2	Electrification of SiC heating element (inside reactor) washcoated with Ni-based catalyst	$CH_4/H_2O/Ar$ =10/30/70; GHSV = 182 h⁻¹	X_{CH_4} = ~70% at 790°C	10
3	Electrification of FeCrAl-alloy (inside reactor) coated with $LaNi_{0.95}Ru_{0.05}O_3$ catalyst	$CH_4/CO_2/N_2$ = 1/2/7; GHSV = 5470 h⁻¹	X_{CH_4} = 29.4% at 900°C	11
4	Electrification of FeCrNi alloy (inside reactor) coated with Ni-based catalyst	$CH_4/H_2O/N_2$ = 1/3/2; GHSV = 157,000 cm³/h/g_cat	X_{CH_4} = 97% at 700°C	12
5	Electrification of SiSiC foam (inside reactor) washcoated with Rh-based catalyst	CH_4/H_2O = 1/4.1; GHSV = 150,000 cm³/h/g_cat	X_{CH_4} = 96% at 700°C	This study

Abbreviation: GHSV = gas hourly space velocity.

reforming feed up to 750°C. This result rules out the possibility that the adopted SiSiC foam works as a catalyst for the MSR reaction.
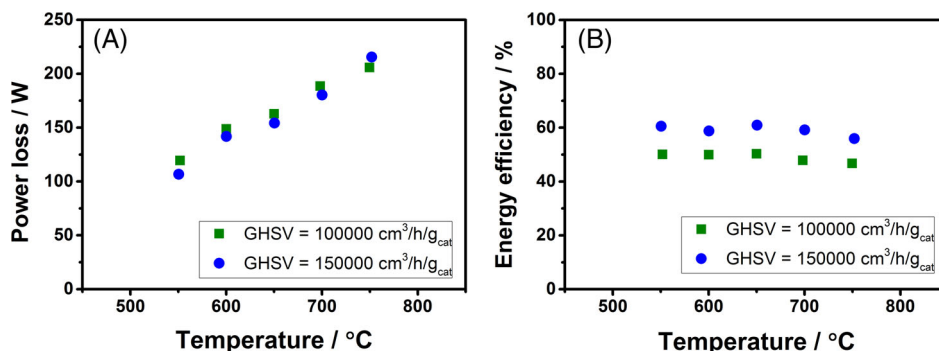
As for the catalyst washcoated SiSiC foam, the experimental methane conversions are plotted against the measured T_{down} temperatures in Figure 6A. For both feed conditions, full methane conversion was approached above 700°C. This is one of the highest conversions (~96%) reported so far for electrified MSR, regardless the specific space velocity adopted in different works (see the detailed

comparison in Table 3). Zhou et al.[12] reported a high methane conversion of 97% at 700°C during eMSR over a Ni-impregnated plate-type alumina support (FeCrNi alloy interlayer as Joule heating substrate). However, the employed plate support exhibited a very low hydrothermal stability, that is, its surface area decreased to only 36% of the initial value after hydrothermal treatment at 700°C for 50 h, which limits its industrialization. The methane conversions measured at the space velocity of 100,000 $cm^3/h/g_{cat}$ are close to equilibrium, indicating that the system works in the thermodynamic regime (Figure 6A). Below 600°C, methane conversions slightly below the equilibrium conversion were observed for the high space velocity condition. This shows that the system works in the kinetic controlled regime, with the lowest conversion of 54% obtained at 550°C. As the result of a highly MSR active Rh/Al_2O_3 catalyst, as well as the adopted moderate experimental conditions, that is, 550°C–750°C and a high S/C ratio of 4.1:1, no coke formation was observed under the investigated conditions. The catalyst-coated SiSiC foam exhibited reasonable stability when operated under the reactive conditions of this study. The long-

term stability of the proposed e-MSR system will be explored in the future. To better understand the overall input–output relationship of the eMSR system, the measured methane conversions are plotted as a function of the input power in Figure 6B.

Interestingly, the conversion performances in the present eMSR system is superior to the conventional oven-heated processes reported from our previous study, where a methane conversion of only 89% was obtained at an oven temperature of 700°C, with a GHSV of 26,000 $cm^3/h/g_{cat}$.[19] This could be explained by the more uniform temperature distribution in the electrified system. However, further studies are necessary to fully characterize the temperature distribution in the new reactor system.

Figure 7 shows the hydrogen productivity obtained from the catalytic tests in the present work. It is apparent that operating at the higher space velocity resulted in a higher hydrogen productivity, which, however, approached a plateau once full methane conversion was achieved. The highest hydrogen productivity of 94 $Nm^3/kg/h$ was measured at 750°C, GHSV = 150,000 $cm^3/h/g_{cat}$. In general, the hydrogen productivity based on reactor volume achieved in this preliminary study is comparable to that obtained by Wismann and coworkers.[13] It can be significantly improved, however, by optimizing both the design parameters of the reactor, for example, geometry of the electrically conductive substrate and thickness (specific load) of the catalyst coating, and the operating conditions of the process, such as temperature, pressure, and steam/carbon ratio.

Figure 8A shows the system power loss, calculated by subtracting the process heat duty Q (Table 2) from the input power P according to Equation 8. The power loss is proportional to the T_{down} temperature and is independent of the gas feed flow (Figure 8A), suggesting that, likely, the source of loss is thermal dissipation via heat conduction in the stainless-steel tube that can act as a heat sink: indeed, despite the thermal insulation applied, the tube ends were still very hot. The increasing trend of power loss with temperature implies that once almost full methane conversion was reached, further temperature increase did not significantly change the process enthalpy duty, thus resulting in a decrease of the energy efficiency, as shown in Figure 8B.

FIGURE 7 Hydrogen productivity as a function of measured T_{down} temperature during the eMSR process. Experimental conditions: 1% Rh/Al_2O_3 washcoated on SiSiC foam with a catalyst loading of 2.2 g, a feed mixture of CH_4 and H_2O with steam to carbon ratio (S/C) of 4.1:1, GHSV of 100,000 (green squares) and 150,000 $cm^3/h/g_{cat}$ (blue circles). eMSR, electrified methane steam reforming; GHSV, gas hourly space velocity

FIGURE 8 Power loss and energy efficiency performance of the novel eMSR reactor configuration: (A) power loss as a function of measured T_{down} temperature during the eMSR process; (B) energy efficiency as a function of measured T_{down} temperature during the eMSR process. Experimental conditions: 1% Rh/Al_2O_3 washcoated on SiSiC foam with a catalyst loading of 2.2 g, a feed mixture of CH_4 and H_2O with steam to carbon ratio (S/C) of 4.1:1, GHSV of 100,000 (green squares) and 150,000 $cm^3/h/g_{cat}$ (blue circles). eMSR, electrified methane steam reforming; GHSV, gas hourly space velocity

On the other hand, the invariance of power loss with the feed flow rate results in an increase of energy efficiency when the system is operated at higher space velocities. In fact, the higher space velocity condition exhibits an energy efficiency of 61% at 650°C, in comparison to 50% obtained for the low space velocity condition (Figure 8B). This result is consistent with previous study by Badakhsh et al.,[24] as well as with our modeling of electrified steam reforming.[25] The obtained values are remarkable when considering that the small size of present system promotes thermal losses. Higher energy efficiencies can be expected when operating electrified reformers with a bigger size.

As a result of a higher energy efficiency, the eMSR system exhibited lower energy consumption per unit of hydrogen production when operated at the higher space velocity (Table 2), that is, 2.0 $kWh/Nm^3_{H_2}$ at 650°C, GHSV = 150,000 $cm^3/h/g_{cat}$. This is markedly lower than the specific energy consumption typically reported for the electrolyzers (3.8–4.4 $kWh/Nm^3_{H_2}$).[36]

The power density of the eMSR system was also evaluated and the highest value of 6.15 MW/m^3 was obtained when the reactor was operated at the higher space velocity at 750 °C. The system can operate at higher power densities, and this possibility will be explored in the future. Moreover, different from conventional fuel fired reformers, the proposed foam-based eMSR system enables to completely eliminate the CO_2 emissions from fuel combustion when driven by renewable electricity. As an environmental benefit, a CO_2 reduction up to 50% can be expected compared with current industrial reformers.[13]

4 | CONCLUSIONS

In this study, we demonstrate a novel reactor configuration for the direct electrification of MSR for low-carbon hydrogen production, based on a Rh/Al_2O_3 washcoated Si-infiltrated silicon carbide foam. Thanks to the interconnected geometry and the proper bulk resistivity of the SiSiC foam, the structured catalyst could be directly heated by the Joule effect (ohmic heating). As a result of strongly reduced heat and mass transfer limitations, methane conversions approaching equilibrium were obtained across a range of conditions, with almost full methane conversion at temperatures above 700°C. The foam-based eMSR system showed a high energy efficiency of 61% and a low specific power consumption (2.0 $kWh/Nm^3_{H_2}$) for hydrogen production at 650°C, GHSV = 150,000 $cm^3/h/g_{cat}$. When driven by renewable electricity, such a reactor configuration promises a high potential to reduce CO_2 emissions in hydrogen production. Further experimental testing, combined with numerical simulations, is ongoing to fully rationalize the proposed new eMSR system.

AUTHOR CONTRIBUTIONS
Lei Zheng: Data curation (equal); formal analysis (equal); investigation (equal); writing – original draft (lead). **Matteo Ambrosetti:** Conceptualization (equal); investigation (equal); writing – review and editing (equal). **Daniele Marangoni:** Conceptualization (equal); resources (equal). **Alessandra Beretta:** Conceptualization (equal); supervision (equal); writing – review and editing (equal). **Gianpiero Groppi:** Conceptualization (equal); supervision (equal); writing – review and editing (equal). **Enrico Tronconi:** Conceptualization (equal); funding acquisition (lead); project administration (lead); writing – review and editing (equal).

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