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Investigation of catalyst performance and microstructured reactor configuration for syngas production by methane steam reforming

Eyup Simsek, Ahmet K. Avci, Z. Ilsen Önsan*

Department of Chemical Engineering, Bogazici University, Bebek 34342, Istanbul, Turkey

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ABSTRACT

This work involves comparative investigation of two catalytic microchannel configurations for synthesis gas generation by methane steam reforming. In the first configuration, catalyst is in the form of a layer which is coated onto the microchannel wall, while the second one is defined by the packing of particulate catalyst into an empty microchannel of the same dimension. Comparison between these geometries is carried out for four different catalysts – Rh, Ru, Pd, Ni – all of which are supported on alumina, and involves testing of different reaction temperatures (873, 923, 973, 1023 K) and steam-to-carbon ratios (2.5, 3.0, 3.5) for each catalyst through a parametric approach. Compared with the packed version, wall-coated microchannel geometry leads to higher methane conversions and syngas production rates as well as lower H_2/CO ratios in the entire parameter and catalyst range investigated. Rh is the best catalyst in terms of activity and H_2 and CO throughputs, while Ni gives the highest hydrogen selectivity. The results indicate the possibility of reducing H_2/CO ratio in methane steam reforming by the use of reformers characterized by wall-coated microchannels.

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1. Introduction

Increasing demands in running chemical productions at lower capital and operating expenses have recently built up interest in novel approaches such as process intensification [1,2]. Various strategies of intensification can be realized either by integrating chemical reactions with unit operations such as separation and heat exchange, or, more recently, by miniaturizing the characteristic flow paths into well-defined structured geometries [3]. The latter approach of intensification can bring added values like the possibility of operating in narrow control limits and of increasing the throughput by numbering up the flow paths which eliminate complexities associated with traditional scaling-up efforts [3–5].

Studies addressing the intensification of flow paths have led to the design and analysis of microchannel reactors. These miniature devices involve parallel, identical channels with characteristic dimensions between $\sim 10^{-6}$ and 10^{-3} m and laminar flow conditions [3–5]. They are constructed mostly using metallic substrates to give surface areas in the 1×10^4–5×10^4 m^2/m^3 range, which are ca. 50–100 times higher than those of their conventional packed-bed counterparts [4]. Presence of high surface areas, sub-millimeter dimensions and use of metallic materials favor rapid and uniform distribution of heat to the entire catalyst, which can be either coated as a layer on the interior channel walls or packed into the channels in particulate form [3–5]. Effective heat transfer is essential for highly endothermic and exothermic catalytic processes demanding precise control of temperature and product distribution.

Catalytic steam reforming of natural gas, composed mostly of methane, is the conventional process used to produce hydrogen at industrial scale [6]:

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^\circ = 206.2\,\text{kJ/mol} \tag{1}$$

Product distribution of steam reforming is affected by the water–gas shift reaction, which is at equilibrium under the reaction conditions [6]:

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^\circ = -41.2\,\text{kJ/mol} \tag{2}$$

Steam reforming runs in tubular reactors packed with Ni-based catalysts. The process is endothermic and requires significant quantities of external heat which is supplied either by direct firing or by heat exchange with a hot stream [6,7]. Distribution of external heat to the catalyst bed has direct impact on the process efficiency. Due to the limited heat transfer characteristics of packed beds, external heat may not be ideally transferred to the catalysts and local catalyst temperatures may be lower than the desired values. This phenomenon affects the SR product spectrum in favor of H_2-rich production; CO produced by Reaction (1) is converted to CO_2 and H_2 by the exothermic water–gas shift (Reaction (2)). However, the situation is not suitable for syngas production at H_2/CO ratios less than 3.0. At this stage, use of microchannel reactors can offer a potential

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* Corresponding author. Tel.: +90 212 3596412; fax: +90 212 2872460.
E-mail address: onsan@boun.edu.tr (Z.I. Önsan).

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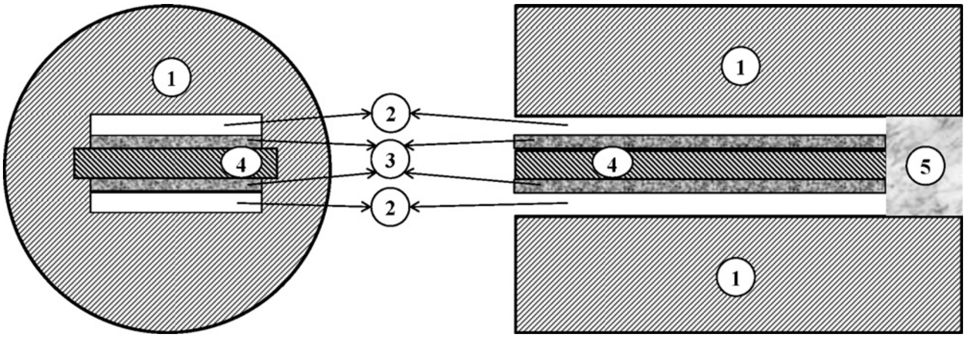

Fig. 1. Top (at the left) and cross-sectional (at the right) views of the coated microchannel configuration (1: engineered metal housing; 2: open microchannels; 3: coated catalyst layers; 4: FeCrAlY plate; 5: ceramic wool plug).

solution by providing rapid delivery of external heat to the catalyst, and, at suitable temperature, catalyst, and steam-to-methane feed ratios, can allow steam reforming to produce syngas appropriate for synthetic fuel manufacturing which is conventionally being carried out by autothermal reforming [7].

Methane steam reforming (MSR) in catalytic microchannels was studied by several groups [8–11]. Johnson et al. [9] investigated MSR over Rh-catalyst integrated microchannels. They studied the reaction at high temperatures (up to 900 °C), steam-to-carbon (S/C) molar ratio of 1.0, and a contact time of 27 ms, and observed near equilibrium conversion and selectivity without catalyst deactivation. Similarly, Wang et al. [10] integrated a 10 wt% Rh/MgO–Al_2O_3 catalyst into an engineered microchannel structure and obtained H_2/CO ratios around 3.5, methane conversion and CO selectivity of ca. 60% and 80%, respectively, at a temperature of 900 °C, S/C ratio of 1.0, and a contact time of 27 ms. Ryu et al. [11] washcoated Ni over a FeCrAlY based metal monolith and obtained almost complete MSR conversion at a temperature and gas-hourly space velocity (GHSV) of 700 °C and 9443 h^{-1}, respectively. Combustion assisted reforming of methane, which involves heat exchange between catalytic oxidation and steam reforming in different compartments of the same microchannel reactor volume has also been demonstrated [12–19]. Studies that exploit the differences of microchannel reactors with their conventional packed counterparts are scarce. Wang et al. [10] compared methane steam reforming in a packed bed reactor and in engineered microchannel reactor made by FeCrAlY felt inserts of specific dimensions using the same catalyst, and reported that the latter led to higher methane conversions and CO selectivities. Ryu et al. [11] ran comparable MSR tests over coarsely powdered and wash-coated monolith geometries, both of which contained equal volumes of Ni-based catalyst. They found that the monolith wash-coated Ni-catalyst gave higher methane conversions, and the difference between coated and powdered forms became more significant at GHSV values above 28,000 h^{-1} where no pressure drop was noted for the monolith [11]. Karim et al. [20] studied methanol steam reforming in wall-coated and packed-bed reactors and concluded that wall-coated configuration was free from any transport limitations, whereas packed-bed reactor operation was limited by heat transfer. The importance of heat effects was emphasized by Tadd et al. [21] who compared the performances of microchannel and packed-bed reactor in the autothermal reforming of iso-octane.

A survey of the literature shows that studies addressing MSR in microchannels and their direct comparison with conventional packed-bed reactors are scarce. The major aim of this work was to investigate and compare the MSR performances of precious metal and nickel catalysts for syngas production in two different microchannel reactor geometries, namely wall-coated and packed microchannels. Studies were carried out within a wide test matrix and involved testing of alumina supported 2% (by weight) Rh, 2% Ru and 2% Pd catalysts together with the conventional 10% Ni catalyst at different temperatures (600, 650, 700, 750 °C) and steam-to-carbon ratios (2.5, 3.0, 3.5) through a parametric approach.

2. Experimental

2.1. Catalyst preparation

Catalysts tested in this study are prepared in two different geometric forms, namely particulate and wall-coated catalysts. Preparation of particulate catalysts starts with the preparation of a thermally stable support, δ-Al_2O_3. For this purpose, γ-Al_2O_3 (Alcoa, 279 m^2/g) is first crushed and sieved to 60–80 mesh (180–255 μm) particle size and then subjected to heat treatment, which involved drying of γ-Al_2O_3 at 473 K for 2 h followed by its calcination at 1173 K for 4 h. This treatment leads to the formation of δ-Al_2O_3 which has a lower surface area (82 m^2/g), but also has sufficient thermal stability against MSR conditions [22]. After support preparation, Rh, Ru, Pd and Ni based catalysts, all supported on δ-Al_2O_3, are synthesized by incipient-to-wetness technique with metal loadings of 2% (by weight) for Rh, Ru, and Pd, and 10% (by weight) for Ni. Calculated amounts of the corresponding precursor salts, $Ni(NO_3)_2 \cdot 6H_2O$, $Rh(NO_3)_3$, $Pd(NO_3)_2 \cdot xH_2O$, and $Ru(NO)(NO_3)_3$, all supplied from Sigma–Aldrich, are dissolved in definite amounts of deionized water. Aqueous precursor solutions are then impregnated onto the δ-Al_2O_3 support particles via a peristaltic pump. The resulting slurries, which are formed after ultrasonic mixing of the aqueous solutions and the support under vacuum for 1.5 h, are dried overnight at 393 K and calcined at 773 K for 4 h in the cases of Rh, Ru and Pd, and at 873 K for 4 h in the case of Ni.

The procedure summarized above for the synthesis of particulate catalysts is applied for the preparation of the catalyst layer used in the wall-coated geometry. Instead of starting with alumina particles of 180–255 μm size, the γ-Al_2O_3 (Alfa Aesar) powder with 3 μm particle size is used for synthesizing the catalyst powders. After heat treatment, a given amount of catalyst powder (ca. 0.072 g) is then mixed with a definite amount of deionized water containing a calculated amount of the precursor salt concerned in order to obtain the catalyst slurry by the incipient-to-wetness impregnation technique. After this step, the slurry is carefully placed, i.e. coated, as a thin layer on both sides of a metallic plate by using a thin blade. The metallic plate used is made of FeCrAlY alloy (Goodfellow) and has dimensions of 2 mm × 5 mm × 25 mm (height × width × depth). Before the slurry is coated, the plates are heat treated at 1173 K for 4 h with a heating rate of 20 K/min for obtaining a native, tortuous surface composed of Al_2O_3, which is reported to improve the adhesion of the coating [23]. The catalyst slurry coated plate is then dried at 393 K for 2 h, and finally, calcined at 773 K for 4 h in the cases of Rh, Ru and Pd, and at 873 K for 4 h in the case of Ni, using heating rates of 5 K/min.

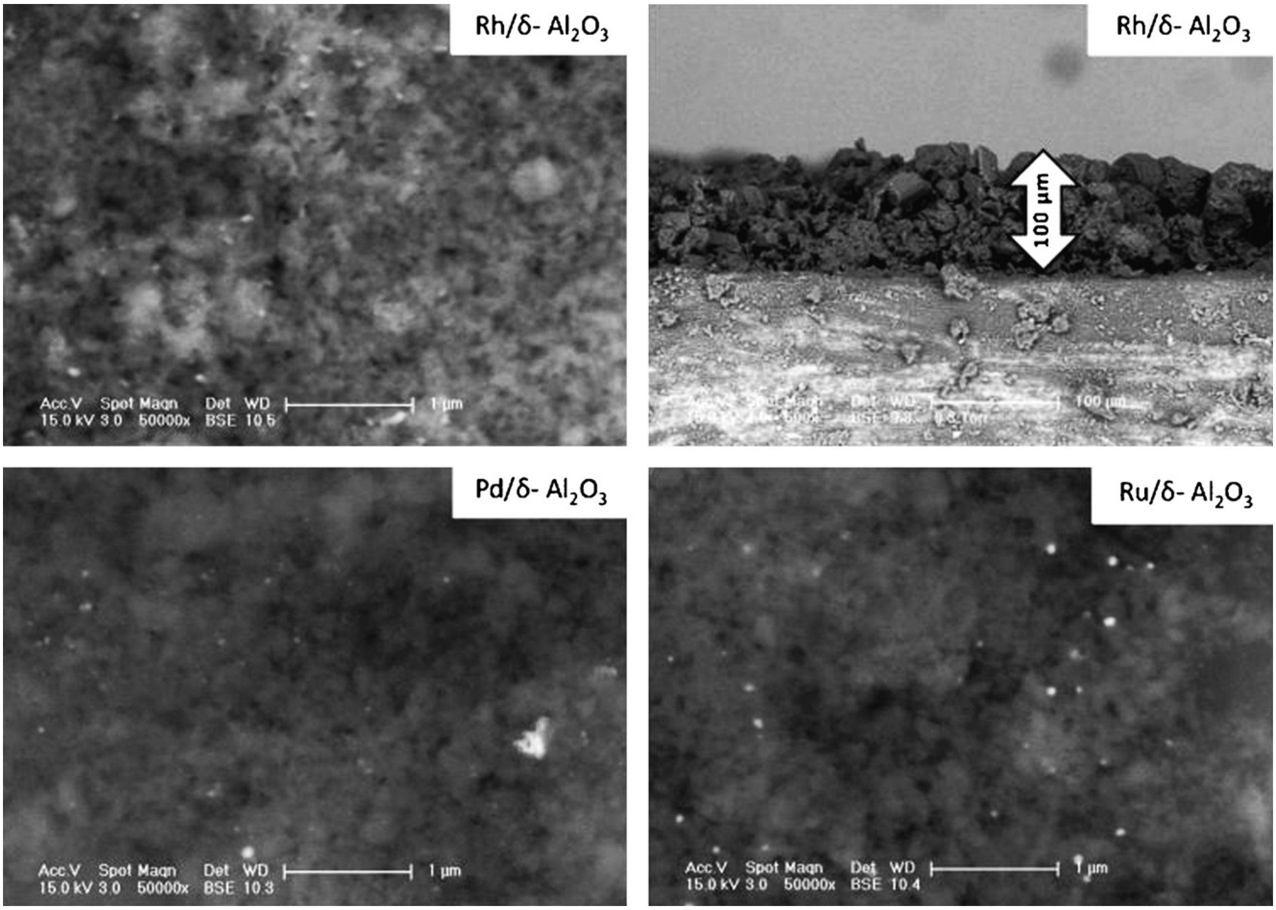

Fig. 2. ESEM micrographs (50,000×) of 2 wt% precious metal containing catalysts (Rh, Pd, Ru) and cross-sectional ESEM image (500×) of the coated catalyst layer obtained in preparing the 2 wt% Rh catalyst.

The microchannels in the reactor are formed by using a cylindrical engineered metal housing made of 310-grade stainless steel with external dimensions of 18.6 mm × 30 mm (outer diameter × length) (Fig. 1). The interior of the housing is shaped with the wire electro discharge machining technique, such that the coated plate is inserted into the central part with 0.5 mm fitting at each side to give two wall-coated catalytic microchannels, each having dimensions of 0.75 mm × 4 mm × 25 mm (height × width × depth). After insertion, the catalyst layers at the first and last 0.5 mm zones of the plate are scraped to overlap between the plate and grooves and to give a total remaining coating mass of 0.065 g (Fig. 1). In this configuration, height of a microchannel (0.75 mm) includes the thickness of the open channel and the coated catalyst layer, the latter being close to 0.1 mm (Fig. 2) as measured by the cross-sectional ESEM images of the coated plates (Section 3.1). In order to prevent the movement of the plate, a plug of ceramic wool (Shimadzu) is placed into the last 5 mm gap between the end of the plate and the housing (Fig. 1).

The same engineered housing is used to configure the packed microchannels. In this case, an uncoated plate is inserted into the central part of the housing and supported with a ceramic wool plug that is put into the last 5 mm gap between the end of the plate and the housing, as shown in Fig. 1. The resulting gaps form two microchannels, each having dimensions of 0.75 mm × 4 mm × 25 mm (height × width × depth). These microchannels are filled with a total amount of 0.065 g of the particulate catalyst, such that each channel contains an equal catalyst mass of 0.0325 g.

2.2. Activity tests

The housing, either with coated or packed catalyst, is placed into the center of a down-flow 20 mm-ID cylindrical quartz tube involving a horizontal hollow ring, whose dimensions are arranged to ensure sufficient overlap with the metal parts of the housing. The designed overlap keeps the housing fixed at the desired position and helps in eliminating any bypass stream through the gap between the tube and the housing. The possibility of bypass is further reduced during the experiments due to the thermal expansion of the metal housing at high temperatures that closes the gap. The temperature at the tube center, i.e. of the catalytic microchannels, is controlled and measured to ±0.1 K by a Shimaden FP-21 programmable controller and a K-type sheathed thermocouple, the latter being placed in the center of the furnace adjacent to the microchannels. Position of the tube center and hence of catalytic microchannels are adjusted to remain within the 10 cm long constant temperature zone of the tube furnace. Blank tests did not indicate any activity due to the metal housing, plate or ceramic wool under the pertinent reaction conditions.

Methane steam reforming experiments are carried out at 873, 923, 973 and 1023 K and at atmospheric pressure with steam-to-carbon-ratios of 2.5, 3.0 and 3.5. Steam-to-carbon (S/C) ratio is defined as the ratio of the number of moles of steam to that of methane at the inlet. Before the reaction tests, the catalysts are reduced in situ by 25 $cm^3\ min^{-1}$ of pure hydrogen flow at 1073 K for 2 h. An Aalborg GFC171S series mass flow controller is used to maintain constant flow of hydrogen. Flow of other gases, methane and nitrogen, are measured and controlled by Omega 5878 series mass flow controllers. Deionized water is metered at constant flow rates by a Jasco PU-1580 intelligent HPLC pump through a separate line that is kept at 398 K by a heating-tape/temperature controller system to ensure vaporization. All gas and steam flow rates are normalized to 298 K and 1 atm. During the experiments, total flow rates and catalyst weights in both reactor configurations are kept constant at 90 $cm^3\ min^{-1}$ and 0.065 g, respectively. In testing the effect of temperature, feed composition is fixed at a volumetric CH_4:H_2O:N_2 ratio of 10:25:65, while the studies on the effect of the S/C ratio were conducted by changing the steam and nitrogen flow rates so as to keep the methane and total flow rates constant at 9 and 90 $cm^3\ min^{-1}$, respectively. The same plan of experiments is applied to both coated and packed microchannel configurations, which are compared on the basis of identical contact time defined as the ratio of catalyst weight to inlet methane flow rate ($W_{cat}/F_{CH4,o}$) equal to 7.22 mg min cm^{-3} (which corresponds to ca. 75 ms based on total microchannel volume including the catalyst). This definition of contact time ($W_{cat}/F_{CH4,o}$) is preferred since it is independent of whether the catalyst is in the form of particles or is wall-coated [24]. All results reported in this study are based on product data collected 90 min after the start-up of the MSR reaction; each experimental run is conducted for a period of 3–9 h.

Reactant and product analysis is conducted using a Shimadzu GC-8A gas chromatograph that is equipped with a Molecular Sieve 5A packed column and a thermal conductivity detector held at 333 K and 363 K, respectively. The products, H_2, N_2, CH_4 and CO, are detected under argon carrier gas flow of 50 $cm^3\ min^{-1}$. Since the molecular sieve column is deactivated by water vapor, two salt-ice cold traps held at 273 K in Dewar flasks were placed before the GC unit to remove the water vapor in the product mixture. Reactant and product streams are sampled and injected using an on-line six-way valve. Research grade gases of high purity (H_2, N_2, CH_4, Ar, He > 99.99%, supplied by Linde) are used in reaction tests and GC analysis.

3. Results and discussion

3.1. Catalyst characterization

The precious metal catalysts, 2% Rh, 2% Ru and 2% Pd, selected for investigation along with the conventional 10% Ni were all supported on δ-Al_2O_3 in both particulate and coated catalysts by the incipient-to-wetness technique, which is the best method for achieving targeted active metal loadings. Scanning electron microscopy coupled with energy dispersive X-ray analysis (Philips XL30 ESEM-FEG/EDAX) system was used for quantitative analysis and X-ray mapping of various freshly reduced samples, and several regions on each sample, to determine average metal loadings. The targeted and achieved metal loadings of particulate and coated catalysts are presented in Table 1, while representative ESEM images of 2% precious metal containing catalysts are shown in Fig. 2, together with the cross-sectional image of the coated catalyst layer obtained in preparing the 2% Rh catalyst. EDX mapping results (not provided here) clearly indicate uniform metal dispersion, and actual metal loadings quite close to the targeted values for all catalysts (Table 1). The cross-sectional ESEM image of freshly coated 2% Rh/δ-Al_2O_3 layer is representative of the uniform catalyst layer thickness attained in the preparation of each coated catalyst.

Table 1
Targeted and achieved metal loadings of particulate and coated catalysts obtained from EDX mapping analyses.

Catalysts	Target metal loading (wt%)	Actual metal loading – Coated form (wt%)	Actual metal loading – Particulate form (wt%)
Rh/δ–Al_2O_3	2	1.97	1.99
Ru/δ–Al_2O_3	2	2.11	2.52
Pd/δ–Al_2O_3	2	2.50	2.27
Ni/δ–Al_2O_3	10	8.29	10.13

3.2. Microchannel reactor configuration

Two major groups of experiments were conducted using δ-Al_2O_3-supported 2% Rh, 2% Ru, 2% Pd, or 10% Ni catalysts that were either coated on microchannel walls or packed into microchannels as 180-255 μm particles. The inlet methane concentration was fixed at 10 mol% in all the experiments. For all catalysts, reactor performances were compared at constant contact time, that is, by keeping the $W_{cat}/F_{CH4,o}$ ratio constant at the same value of 7.22 mg min cm^{-3} in both coated and packed microchannel reactors. In the first group of experiments, the reaction temperature was varied keeping all other reaction parameters constant, and the variable in the second group of experiments conducted was the steam-to-carbon (S/C) molar ratio.

3.2.1. Effect of reaction temperature

The effect of reaction temperature on MSR was studied in the 873 to 1023 K temperature range by both individual experiments using fresh catalyst samples and by group experiments starting

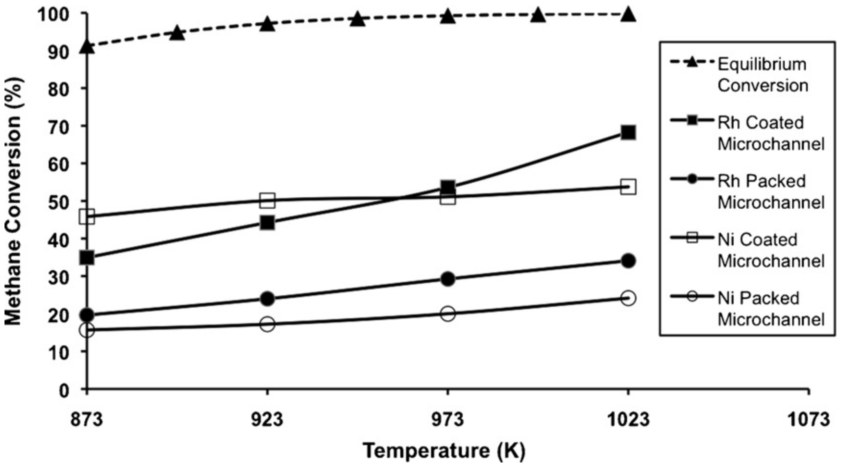

Fig. 3. Effect of temperature on methane conversions obtained at S/C = 2.5 over 2 wt% Rh and 10 wt% Ni catalysts in coated and packed microchannel configurations and on corresponding equilibrium conversions.

Table 2
Effect of reaction temperature on methane conversion (x_{CH4}), molar H_2/CO ratio in the product stream, and production rates of H_2 (r_{H2}) and CO (r_{CO}) in packed and coated microchannel reactors.

Catalyst	T (K)	Packed microchannel				Coated microchannel			
		x_{CH4} (%)	H_2/CO	r_{H2} (μmol min^{-1} mg^{-1})	r_{CO} (μmol min^{-1} mg^{-1})	x_{CH4} (%)	H_2/CO	r_{H2} (μmol min^{-1} mg^{-1})	r_{CO} (μmol min^{-1} mg^{-1})
2 wt% Rh/δ–Al_2O_3	873	19.6	15.4	3.77	0.24	34.9	5.9	5.90	1.00
	923	23.9	9.7	4.22	0.44	44.2	4.4	7.39	1.69
	973	29.3	7.1	4.88	0.69	53.6	4.1	8.97	2.17
	1023	34.1	6.1	5.80	0.96	68.2	3.4	11.31	3.32
2 wt% Ru/δ–Al_2O_3	873	10.4	12.8	1.46	0.11	31.3	8.1	5.41	0.67
	923	13.4	7.7	1.85	0.24	35.9	5.9	6.10	1.03
	973	14.1	7.3	2.05	0.28	38.7	5.6	6.70	1.20
	1023	15.8	7.3	2.24	0.31	38.8	5.2	7.69	1.48
2 wt% Pd/δ–Al_2O_3	873	12.2	11.8	1.99	0.17	28.8	5.8	4.29	0.74
	923	16.7	7.1	2.79	0.39	41.9	4.6	6.62	1.43
	973	21.1	6.9	3.58	0.51	55.1	4.5	8.38	1.85
	1023	25.5	5.6	4.28	0.76	55.9	4.6	9.08	1.98
10 wt% Ni/δ–Al_2O_3	873	15.7	27.3	2.29	0.08	45.8	10.4	7.61	0.73
	923	17.2	14.0	2.55	0.18	50.1	7.4	8.03	1.09
	973	19.9	10.8	2.93	0.27	51.1	6.7	8.53	1.28
	1023	24.2	8.4	3.5	0.42	53.8	6.0	8.42	1.41

from 1023 K going to lower temperatures without removing the catalyst from the reactor. The feed composition was kept constant at an inlet methane concentration of 10 mol% and an S/C molar ratio of 2.5, and a contact time of 7.22 mg min cm^{-3} was used in all experiments. Although the risk of coking on Rh and Ru catalysts is rather low at the temperatures used, the S/C molar ratio was kept above stoichiometric in order to eliminate coke formation on Ni, since the recommended ratios for MSR over Ni are between 2.5 and 3 [6]. The results of individual and group experiments were reproducible. ESEM analyses conducted over the spent catalyst samples did not indicate the formation of any kind of carbonaceous deposits.

The constant $W_{cat}/F_{CH4,o}$ ratio selected (7.22 mg min cm^{-3}) made it possible to keep methane conversion levels well below equilibrium conversions at all temperatures on the catalysts tested in this work and, thus, to easily differentiate between the performances of the two reactor configurations. Moreover, under these conditions, no detectable catalyst deactivation was observed. Methane conversions obtained at an S/C ratio of 2.5 over 2% Rh and 10% Ni catalysts in coated and packed microchannel reactors are presented as a function of reaction temperature in Fig. 3 together with the corresponding equilibrium conversion levels calculated from thermodynamic data using HSC 6.1 computer software. These results demonstrate quite clearly that the coated microchannel reactor gives higher methane conversion levels than the packed microchannel reactor on both 2% Rh and 10% Ni catalysts and reactant conversions remain below equilibrium limits in the entire temperature range considered.

Experimental results obtained for MSR at 873–1023 K with an S/C molar ratio of 2.5 over four catalysts tested in coated and packed microchannel reactors are summarized in Table 2 and Fig. 4. In each case, methane conversion increases with temperature, and conversions are highest over Rh at all temperatures; at 1023 K, methane

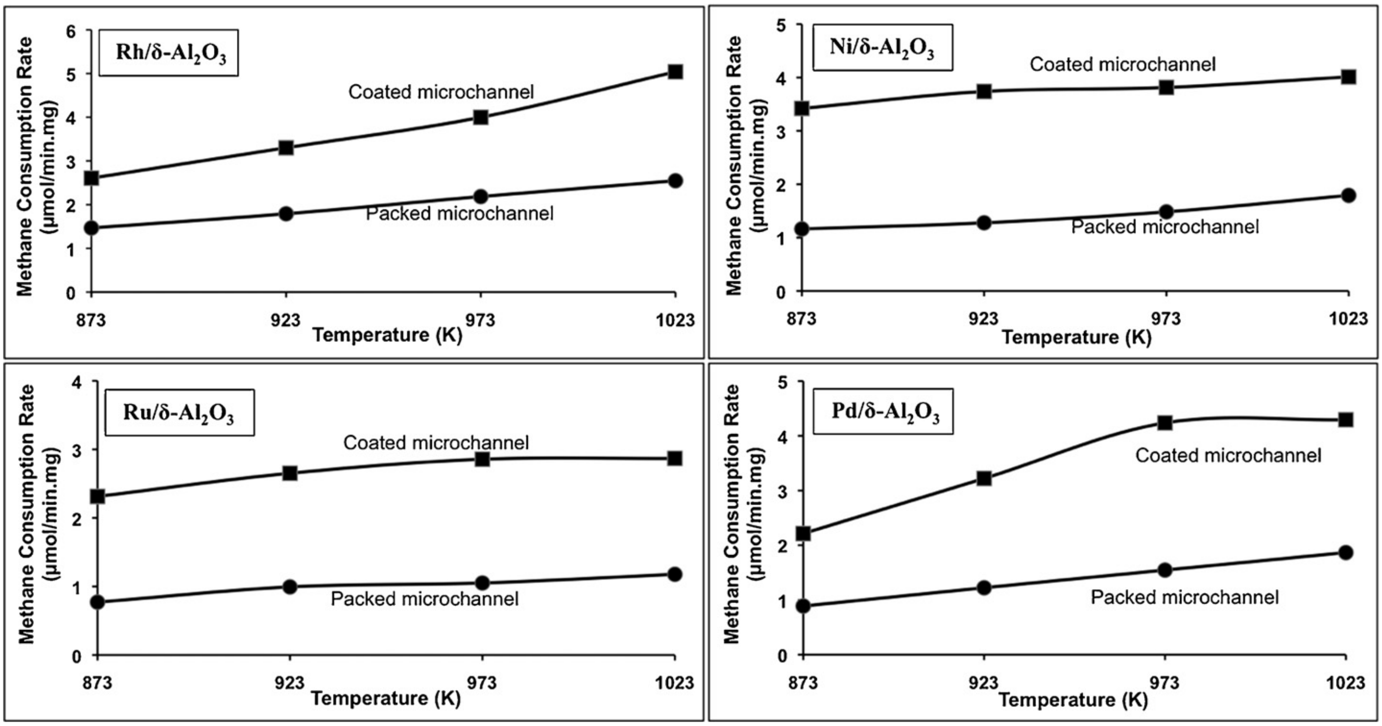

Fig. 4. Effect of temperature on methane consumption rates at S/C = 2.5 over 2 wt% Rh, 2 wt% Pd, 2 wt% Ru and 10 wt% Ni catalysts in coated and packed microchannel reactors.

conversions of 68.2% and 34.1% are achieved in coated and packed microchannels, respectively. In both reactor configurations, catalytic activity decreases in the order 2% Rh > 2% Pd ≥ 10% Ni > 2% Ru; methane conversions and consumption rates over Ni and Pd are quite close to each other at all reaction temperatures. It is observed that, compared to packed microchannels, much higher methane conversion levels and consumption rates as well as higher H_2 and CO production rates are reached in coated microchannels on all the catalysts, which can be attributed to improved heat and mass transfer characteristics of the coated microchannel reactor.

A major parameter for syngas production by steam reforming is the H_2/CO molar ratio obtained in the product stream. Over each of the catalysts tested in the two reactor configurations, H_2/CO molar ratio in the product decreases with increasing temperature; for instance, over Rh, the H_2/CO molar ratio in product decreases from 15.4 to 6.1 in the packed microchannel, and from 5.9 to 3.4 in the coated microchannel, as reaction temperature is increased from 873 to 1023 K. This decrease is more noticeable on the Ni catalyst where the H_2/CO ratio falls from 27.3 to 8.4 in the packed microchannel, and from 10.4 to 5.99, in the coated microchannel. It is remarkable that, on all the catalysts tested, the H_2/CO ratios achieved in coated microchannels are significantly lower than those attained in packed microchannels, and the lowest H_2/CO ratio of 3.4 is obtained at 1023 K on Rh in the coated microchannel reactor. In both configurations, the H_2/CO ratios are higher than 3.0, the stoichiometric value dictated by the MSR (Reaction (1)). The deviations become more significant at low temperatures. These observations indicate the effect of the exothermic water–gas shift, an important side reaction [6], whose impact becomes stronger due to the use of excess steam to keep S/C ratio ≥ 2.5 for preventing carbon formation. According to Le Chatelier's principle, excess steam and lower temperatures favor Reaction 2 in the products direction, which converts CO generated by MSR into H_2 and CO_2, and leads to the highest H_2/CO ratios observed at 873 K (Table 2). This effect becomes less pronounced at higher reaction temperatures at which reverse water–gas shift starts becoming appreciable and H_2/CO ratios start decreasing with temperature, but still remain above 3.0 due to the use of excess steam (Table 2).

An explanation for the higher methane consumption rates and lower H_2/CO ratios achieved in the coated microchannel reactor is suggested by the fact that MSR is thermodynamically favored at high temperatures and high S/C molar ratios in the feed, and therefore, it is greatly influenced by heat and mass transport limitations inherent in packed-bed reactors, which are also subject to wall flow effects. Endothermic nature of the MSR reaction leads to axial and radial temperature gradients in packed beds, and these gradients have a bearing on the product distribution and H_2/CO molar ratio. The results obtained in this work indicate that the coated microchannel reactor can alleviate these transport effects and reduce temperature gradients to provide nearly isothermal conditions in the coated catalyst layer.

3.2.2. *Effect of inlet steam-to-carbon molar ratio*

The effect of the inlet S/C molar ratio on reactant conversion and product distribution in syngas production by MSR was studied in both reactor configurations at 1023 K using a constant inlet methane concentration of 10 mol% and a contact time of 7.22 mg min cm^{-3}. The S/C molar ratio was deliberately kept above stoichiometric to avoid carbon formation and was therefore varied between 2.5 and 3.5.

Experimental results obtained for MSR at 1023 K with S/C molar ratios of 2.5, 3.0 and 3.5 over the four catalysts in coated and packed microchannel reactors are summarized and compared in Table 3. At all S/C molar ratios and on all catalysts, methane conversion levels and consumption rates reached in coated microchannels are much higher than those in packed microchannel reactors. High-

Table 3
Effect of inlet steam-to-carbon molar ratio (S/C) on methane conversion (x_{CH4}), molar H_2/CO ratio in the product stream, methane consumption rate (-r_{CH4}) and production rates of H_2 (r_{H2}) and CO (r_{CO}) in packed and coated microchannel reactors.

Catalyst	S/C	Packed microchannel					Coated microchannel				
		x_{CH4} (%)	H_2/CO	$-r_{CH4}$ (μmol min^{-1} mg^{-1})	r_{H2} (μmol min^{-1} mg^{-1})	r_{CO} (μmol min^{-1} mg^{-1})	x_{CH4} (%)	H_2/CO	$-r_{CH4}$ (μmol min^{-1} mg^{-1})	r_{H2} (μmol min^{-1} mg^{-1})	r_{CO} (μmol min^{-1} mg^{-1})
2 wt% Rh/δ–Al_2O_3	2.5	34.1	6.07	2.55	5.80	0.96	68.2	3.41	5.04	11.31	3.32
	3.0	33.5	6.33	2.67	6.26	0.99	71.6	4.03	5.71	12.53	3.11
	3.5	35.3	6.66	3.10	6.68	1.00	72.7	4.21	6.39	13.34	3.17
2 wt% Ru/δ–Al_2O_3	2.5	15.8	7.31	1.18	2.24	0.31	38.8	5.2	2.87	7.69	1.48
	3.0	18.2	7.26	1.45	2.50	0.34	37.6	6.36	2.94	6.99	1.10
	3.5	20.8	7.47	1.81	2.85	0.38	46.4	5.07	3.87	8.34	1.64
2 wt% Pd/δ–Al_2O_3	2.5	25.5	5.61	1.87	4.28	0.76	55.9	4.60	4.29	9.08	1.98
	3.0	36.9	7.33	2.72	3.30	0.45	55.2	4.88	4.41	9.42	1.93
	3.5	38.7	8.04	3.12	3.69	0.46	56.6	5.04	4.69	10.09	2.00
10 wt% Ni/δ–Al_2O_3	2.5	24.2	8.38	1.79	3.55	0.42	53.8	5.99	4.01	8.42	1.41
	3.0	23.9	8.92	1.91	3.95	0.44	53.9	6.28	4.17	9.25	1.47
	3.5	26.2	9.16	2.30	4.09	0.45	55.2	6.88	4.60	9.91	1.44

est methane conversions are attained over 2% Rh at all S/C ratios, with 35.3% and 72.7% being reached at an S/C ratio of 3.5 in packed and coated microchannels, respectively. In general, methane conversion increases to some extent with increasing S/C molar ratio; however, this trend is not pronounced mainly because MSR is less sensitive to S/C molar ratios above stoichiometric limits where coking is unlikely. There is some fluctuation in data obtained over 2% Ru in the coated microchannel reactor, which may partly be due to the relatively narrow range of S/C molar ratios considered.

The overall increase in the H_2/CO molar ratio in product stream has the following trend: 2% Rh < 2% Pd ≤ 2% Ru < 10% Ni in packed microchannels, which is slightly modified in coated microchannels as 2% Rh < 2% Pd < 2% Ru ≤ 10% Ni. In both cases, Rh is better in terms of CO selectivity while Ni gives the highest H_2 selectivity under the reaction conditions used in this work, although H_2 and CO production rates over Rh are the highest.

4. Conclusions

MSR is favored at high temperatures and high S/C molar ratios in the feed. Its endothermic nature leads to axial and radial temperature gradients in packed-bed reactors which require careful heat management. Wall-coated reactor configurations minimize transport resistances and provide uniform temperature distribution in the catalyst layer. In order to benefit from the improvements offered by such reactors, it is crucial to use MSR catalysts with high activity, stability, and coating ability. The MSR performances of precious metal and nickel catalysts, namely 2 wt% Rh, 2 wt% Ru, 2 wt% Pd, and 10 wt% Ni, were investigated and compared in wall-coated and packed microchannel reactors operated at 873–1023 K and S/C ratios of 2.5–3.5, using a fixed inlet methane concentration and identical contact times. Methane conversions and consumption rates, and H_2 and CO production rates, reached in coated microchannels were much higher than those in packed microchannels under the reaction conditions covered for all catalysts. In both cases, H_2 and CO production rates over 2 wt% Rh were the highest. It was found that the H_2/CO molar ratios in coated microchannel product streams are significantly lower than those in packed microchannels, 2 wt% Rh is better in terms of CO selectivity while 10 wt% Ni gives the highest H_2 selectivity. These results indicate the possibility of reducing H_2/CO ratio in MSR by using wall-coated microchannel reformers.

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