

Performance and Controlling Regimes Analysis of Methane Steam Reforming on Ru/-Al<sub>2</sub>O<sub>3</sub> Cordierite Monoliths

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# Performance and controlling regimes analysis of methane steam reforming on Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> cordierite monoliths

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## Abstract

In the frame of methane steam reforming (MSR) process intensification for H<sub>2</sub> production, catalysts based on Ruthenium (Ru) supported on Alumina (Al<sub>2</sub>O<sub>3</sub>) on cordierite monolith have been studied in terms of catalytic performance, mass and heat transfer effects. Firstly, we compared the catalytic activity of Ru and Rh supported catalysts. Secondly, we study the effect of catalyst loading by varying the amount of carrier and active metal phase corresponding to 3.20, 6.45 and 12.89 mg cm<sup>-2</sup>. Then, we evaluated the mass/heat transfer effects and controlling regimes for the best-selected catalyst. Finally, the best-selected catalyst was characterized by means of Brunauer-Emmet-Teller (BET), X-Ray diffraction analysis (XRD) and Field-emission scanning electron microscopy (FESEM). The experiments were carried out in the temperature range of 550 to 850 °C, steam to carbon molar ratio (S/C) of 3.0 and different weight hourly space velocity (WHSV= 750, 1500 and 3000 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). The catalyst with 1.5% Ru on 10% Al (1.5Ru10Al) was found to be the most promising toward the MSR reaction in terms of CH<sub>4</sub> conversion and H<sub>2</sub> production.

This catalyst operates in a mixed regime for all temperature range studied, in which both the kinetic and the intraparticle diffusion co-exist. For the 1.5Ru10Al catalyst, the external thermal effects are important a temperature below 725°C, while that intraparticle heat effects are absent for all the range of temperature studied. An excellent stability of the 1.5Ru10Al catalyst was observed over 70 h of time on stream (TOS) for MSR process.

**Keywords:** mass transfer; heat transfer; hydrogen production; methane steam reforming

## Nomenclature

### *Fluid properties*

$C_{CH_4,in}; C_b$	Methane concentration in feed mixture (bulk) ( $\text{mol}\cdot\text{m}^{-3}$ )
$C_{p_f}$	Heat capacity of the gas mixture ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$C_{p_i}$	Heat capacity of $i$ component ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$C_s$	Methane concentration at catalyst surface ( $\text{mol}\cdot\text{m}^{-3}$ )
$D_{CH_4-mix}$	Diffusivity of $\text{CH}_4$ in gas phase ( $\text{m}^2\cdot\text{s}^{-1}$ )
$D_{CH_4,e}$	Effective diffusivity of $\text{CH}_4$ in coated layer ( $\text{m}^2\cdot\text{s}^{-1}$ )
$D_{CH_4-i}$	Binary diffusion of $\text{CH}_4$ and $i$ gas species ( $\text{m}^2\cdot\text{s}^{-1}$ )
$D_k$	Knudsen diffusion ( $\text{m}^2\cdot\text{s}^{-1}$ )
$h_e$	Heat transfer coefficient of gas mixture ( $\text{W m}^{-2} \text{K}^{-1}$ )
$k_{m,e}, k_G$	Mass transfer coefficient of $\text{CH}_4$ ( $\text{m}\cdot\text{s}^{-1}$ )
$k_{m,app}$	Apparent mass transfer coefficient ( $\text{m}\cdot\text{s}^{-1}$ )
$M_{CH_4}$	Molecular weight of $\text{CH}_4$ ( $\text{kg}\cdot\text{kmol}^{-1}$ )
$M_i$	Molecular weight of $i$ compound ( $\text{kg}\cdot\text{kmol}^{-1}$ )
$M_{mix}$	Molecular weight of gas mixture ( $\text{kg}\cdot\text{kmol}^{-1}$ )
$P$	Transverse Peclet number (m)
$R_g$	Universal gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
$u_o$	Inlet gas velocity ( $\text{m}\cdot\text{s}^{-1}$ )
$v_{CH_4}$	Molar volume of $\text{CH}_4$ ( $\text{cm}^3\cdot\text{mol}^{-1}$ )
$v_i$	Molar volume of $i$ compound ( $\text{cm}^3\cdot\text{mol}^{-1}$ )
$y_{CH_4}$	Mole fraction of $\text{CH}_4$
$y_i$	Viscosity of $i$ compound ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ )
$\mu_i$	Viscosity of $i$ compound ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ )
$\mu_f$	Viscosity of gas mixture ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ )
$\lambda_i$	Thermal conductivity of $i$ component ( $\text{W m}^{-1} \text{K}^{-1}$ )

$\lambda_{mix}$	Thermal conductivity of gas mixture ( $\text{W m}^{-1} \text{K}^{-1}$ )
$\rho_f$	Density of gas mixture ( $\text{kg m}^{-3}$ )

#### *Reaction data*

$F_{tot}$	Total gas flow rate ( $\text{m}^3 \cdot \text{s}^{-1}$ )
$k_{obs}$	Observed 1 <sup>st</sup> order reaction rate constant ( $\text{s}^{-1}$ )
$k_s$	Surface reaction rate constant
$P$	Reaction pressure (kPa)
$r_{CH_4}$	Reaction rate for $\text{CH}_4$ ( $\text{kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )
$R_{CH_4}$	Volumetric reaction rate for $\text{CH}_4$ ( $\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ )
$T$	Reaction temperature (K)
$T_b, T_s$	Temperature in the bulk of the gas phase and surface of the catalyst layer (K)
$T_{b,c}$	Temperature in the bulk of the catalyst layer (K)
$\phi$	Thiele modulus
$H$	Effectiveness factor
$\Delta H_r$	Heat of MSR reaction ( $\text{J mol}^{-1}$ )
$\lambda_{cat}$	Catalyst thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )
$\lambda_e$	Effective thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )

#### *Monolith properties*

$A_{ch}$	Area of a single bare channel ( $\text{m}^2$ )
$A_m$	Monolith area ( $\text{m}^2$ )
$A_{\Omega_e}$	Cross-sectional area of fluid phase ( $\text{m}^2$ )
$A_{\Omega_i}$	Cross-sectional area of catalyst layer ( $\text{m}^2$ )
$d_h$	Hydraulic diameter (m)
$d_f$	Average channel dimension (m)
$D$	Inner length of the channel (m)
$D_m$	Monolith diameter (m)
$GSA$	Geometric surface area ( $\text{m}^2 \cdot \text{m}^{-3}$ )
$l_w$	Channel width (m)
$L_m$	Monolith length and diameter (m)
$n$	Cell density ( $\text{N}^\circ \text{ cell} \cdot \text{m}^{-2}$ )
$P_c$	Interfacial perimeter (m)
$R_{\Omega_e}$	Characteristic length for gas phase (m)
$R_{\Omega_i}$	Characteristic length for coated layer (m)
$\varepsilon$	Voidage of square channel
$\delta_w$	Wall thickness (m)
$\zeta$	Cell density (cpsi)

#### *Coated layer properties*

$k_{m,l}$	Internal mass transfer coefficient (m)
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$r_p$	Pore radius (m)
$S_{BET}$	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )
$V_{BJH}$	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
$\delta_c$	Coated layer thickness (m)
$\varepsilon_c$	Coated layer porosity
$\rho_c$	Coated layer density ( $\text{kg} \cdot \text{m}^{-3}$ )
$\tau_c$	Tortuosity factor

#### *Resistances*

$R_e$	External mass transfer resistance ( $\text{s m}^{-1}$ )
$R_i$	Internal mass transfer resistance ( $\text{s m}^{-1}$ )
$R_r$	Reaction resistance ( $\text{s m}^{-1}$ )
$R_t$	Overall resistance ( $\text{s m}^{-1}$ )

#### *Characteristic times*

$t_c$	Characteristic contact time (s)
$t_d^e$	Transverse diffusion time for the flow area (s)
$t_d^i$	Transverse diffusion time for the coated area (s)
$t_r$	Characteristic reaction time (s)
$t_z$	Longitudinal diffusion time (s)

#### *Dimensionless numbers*

$A$	$D_{\text{CH4-mix}}/D_{\text{CH4,e}}$ ratio
$B$	$R_{Qi}/R_{Qe}$ ratio
$Ca$	Carberry number
$Le$	Lewis number
$Pr$	Prandtl number
$Re$	Reynold number
$Sc$	Schmidt number
$Sh_i, Sh_e$	Internal/external Sherwood number
$Sh_{i\infty}, Sh_{e\infty}$	Asymptotic internal/external Sherwood number
$Sh_{app}$	Apparent Sherwood number
$\beta_{in}, \beta_{ext}$	Dimensionless internal/external Prater number
$\gamma_b, \gamma_s$	Arrhenius number at the bulk and surface of the gas phase
$\chi$	Damkholer for interphase heat transport
$\psi$	Damkholer for intraparticle heat
$x$	Radial coordinate

## **Abbreviations**

BET	Brunauer-Emmet-Teller
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EDX	energy dispersive X-ray
FESEM	field emission scanning electron microscopy
ID	internal diameter
MSR	methane steam reforming
NDIR	near D infra red
S <sub>BET</sub>	specific surface area calculated by BET method
SCS	solution combustion synthesis
S/C	steam to carbon ration
TOS	time on stream
WGS	water gas shift
WHSV	weight hourly space velocity
XRD	X-ray diffraction

## 1. INTRODUCTION

Hydrogen (H<sub>2</sub>) is one of the most abundant elements in the Earth's crust and due to its capability to drive the generation of electricity without emitting harmful pollutants, H<sub>2</sub> is considered as a prominent clean, environmentally benign and safe-to-handle major energy carrier of the future [1, 2]. Nowadays, H<sub>2</sub> is used in several industrial processes such as refining, treating metals, and food processing. In addition, H<sub>2</sub> is an essential building block for the production of ammonia, and thus fertilizers, and of methanol, utilized as a part of the production of many polymers [3–7]. The most important source of H<sub>2</sub> today is natural gas (~97 % of CH<sub>4</sub>) with approximately 80% efficiency. In fact, more than 90% of the world's H<sub>2</sub> is produced by steam reforming (SR), being the most viable option for supporting a future hydrogen economy [8, 9]. Methane steam reforming (MSR) is a highly endothermic reaction (Reaction 1) accompanied mainly by the side reaction of the water gas shift (WGS), which is slightly exothermic (Reaction 2):



To be feasible at relatively low pressure and temperature ( $T < 1000$  °C,  $P < 5$  bars), these reactions are carried out in the presence of a catalyst. Nickel-based catalysts are actually the most widely used for industrial reforming processes because of their high availability and low cost [8–10]. However, the catalytic activity gradually decreases because of carbon deposition and sintering of Ni. Catalyst systems based on noble metals have been extensively studied by many researchers, giving rise to excellent catalytic performances towards MSR processes [11, 12]. Noble metals such as Ru, Rh, Pd, Pt, and Ir have a higher barrier for carbon formation during operation than Ni. Particularly, whiskers carbon formation (caused by carbon deposition) can be problematic at severe condition for an effective performance of the catalyst [13]. Moreover, the catalyst may eventually break down [14]. Among

the noble metals, Ru and Rh are the most active metals with comparable performance, while Ru is the most promising candidate due to its lower price [11–15]. On the other hand, the nature of the support in MSR may also have a significant impact on the catalytic activity. Carrier materials for MRS catalysts require high specific surface area, wider pore structure easily accessible for gaseous transport, and thermal stability at high temperature ( $< 1000\text{ }^{\circ}\text{C}$ ), even in the presence of steam [16]. Alumina ( $\text{Al}_2\text{O}_3$ ) is widely used as catalyst carrier because it is inexpensive, reasonably thermally stable and can provide a wide range of specific surface area and porosity through its different phases [17, 18]. Ferreira-Aparicio et al. [19] investigated the role of  $\text{Al}_2\text{O}_3$  support on the catalytic activity of Ru catalysts during MSR. They found that surface hydroxyl groups play a main role in the catalyst's resistance to deactivation. In the same way, Berman et al. [20] reported that during 10 days of operation of 1 wt.% Ru/ $\gamma\text{-Al}_2\text{O}_3$  catalyst in the temperature range of 600–900  $^{\circ}\text{C}$ , the activity was stable without carbon depositions and change of mechanical properties of the catalyst.

Nowadays, research on MSR reaction is mainly devoted to improve the catalyst performance by producing as much  $\text{H}_2$  as possible. Recently, the attention is focused on structured systems with active components supported on different configurations such as monoliths, foams, and honeycombs [16, 21–24]. In particular, monolith catalysts have been widely used in many applications due to for their excellent mechanical and chemical durability, high geometric surface area, rapid response to transient operation, low pressure drop and smaller sizes than reactors with traditional catalyst pellet materials. Furthermore, monolith reactors offer other advantages such as reduced capital cost, smaller footprints, and potentially easier transportation compared to fixed-bed reactors [25–27].

Several studies have shown that structured catalysts improve heat and mass transfer mechanisms between the fluid and solid phases. Especially, for endothermic process, high thermal conductive supports allow optimal thermal management in the catalytic volume maximizing heat transfer from the heating medium to the catalytic volume and reducing the temperature gradient due to the endothermicity of the reaction [28]. According to Tronconi et al. [28, 29], the effective thermal conductivity of a structured catalysts depends fundamentally on the conductivity of the substrate and that of the solid carrier deposited on the substrate. On the other hand, it is well known that in many heterogeneous catalytic reactions, the overall rate of reaction is often limited by mass transfer processes, which include both the internal diffusion (at intermediate temperatures) and external diffusion (at sufficiently high temperatures) of components into and out of the catalyst, especially for highly exothermic or endothermic reactions such as combustion or steam reforming [23, 24, 30, 31].

In the present work, we investigated the catalytic performance towards MSR of Ru and Rh on  $\gamma\text{-Al}_2\text{O}_3$  catalysts supported on ceramic cordierite monoliths of square channel. Firstly, we compared the catalytic performance in terms of  $\text{CH}_4$  conversion,  $\text{H}_2$  production, CO selectivity and  $\text{H}_2/\text{CO}$  molar ratio of Rh and Ru supported on  $\gamma\text{-Al}_2\text{O}_3$ . Secondly, we study the influence of the catalyst loading by varying the amount of carrier and active metal phase. Then, we evaluated the different controlling regimes (kinetic, intraparticle, or interphase diffusion control)

and heat transfer effects for the best catalyst. All cordierite monoliths were coated by solution combustion synthesis. Finally, we evaluated the stability of the catalyst on the best-selected one.

## 2. METHODS

### 2.1. Chemicals and monoliths

Aluminium (III) nitrate nonahydrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $\geq 98\%$  purity), ruthenium (III) nitrosyl nitrate,  $6\text{Ru}(\text{NO})(\text{NO}_3)_3$  ( $\geq 98\%$  purity), rhodium(III) chloride,  $\text{RuCl}_3$  ( $\geq 98\%$  purity), urea,  $\text{CH}_4\text{N}_2\text{O}$  ( $\geq 99\%$  purity) were purchased from Sigma–Aldrich. All aqueous solutions were prepared using ultrapure water (Millipore Milli-Q system with resistivity  $> 18 \text{ M}\Omega \text{ cm}$ ). For catalytic activity tests, pure  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2$  gasses (purity 99.999%) were supplied in cylinders provided by SIAD S.p.A. (Italy) and used as received.

Ceramic monoliths of square channel (100 cell per  $\text{in}^2$ ) made of cordierite in dimensions of 40 mm diameter by 30 mm were provided by Chauger Honeycomb Ceramics Co. (Taiwan).

### 2.2. Catalysts preparation

Before the catalyst deposition, cordierite monoliths were cleaned in an ultrasonic bath with a water/acetone solution (50/50 vol.%) for 30 min and dried at  $120^\circ\text{C}$  for 2 h. The catalytic layer based on Ru supported on  $\gamma\text{-Al}_2\text{O}_3$  was coated by *in-situ* solution combustion synthesis (SCS) following the detailed procedure discussed in our previous work [32]. Briefly, the necessary amounts of aluminum nitrate, ruthenium nitrosyl nitrate as precursors and urea as fuel were dissolved in aqueous solution (3 M) under vigorous stirring. The ratio between the amount of urea used and the stoichiometric amount ( $\Phi$ ) was equal to 1 [33, 34]. Then, each monoliths was dipped in the aqueous solution for 2-3 min and then introduced into a muffle furnace preheated at  $600^\circ\text{C}$  for 10 min, where the combustion reaction occurred, letting the formation of the catalytic layer, and rapidly cooled down to room temperature in few minutes. The operation was repeated until the design weight of  $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$  was reached. Finally, the coated monoliths were calcined at  $600^\circ\text{C}$  for 2 h in static air.

For comparison of the catalytic performance, Rh-based catalysts were also prepared with the same procedure by using the corresponding nitrate of the active metal. A set of X wt.% ( $X = 1.5$  and 3) of metal active phase (Ru, Rh) supported on  $\gamma\text{-Al}_2\text{O}_3$  (with varying carrier loadings equal to 5, 10 and 20 wt.% compared to the weight of the monolith) were prepared, according to Table 1.



Metal	Carrier	Catalyst	Abbreviation
1.5% Ru	5% Al <sub>2</sub> O <sub>3</sub>	1.5% Ru / 5% Al <sub>2</sub> O <sub>3</sub>	1.5Ru5Al
3.0% Ru	5% Al <sub>2</sub> O <sub>3</sub>	3.0% Ru / 5% Al <sub>2</sub> O <sub>3</sub>	3Ru5Al
1.5% Ru	10% Al <sub>2</sub> O <sub>3</sub>	1.5% Ru / 10% Al <sub>2</sub> O <sub>3</sub>	1.5Ru10Al
1.5% Ru	20% Al <sub>2</sub> O <sub>3</sub>	1.5% Ru / 20% Al <sub>2</sub> O <sub>3</sub>	1.5Ru20Al
1.5% Rh	10% Al <sub>2</sub> O <sub>3</sub>	1.5% Ru / 10% Al <sub>2</sub> O <sub>3</sub>	1.5Rh10Al

**Table 1.** List of catalyst prepared by varying metal and carrier load.

### 2.3. Catalytic tests

The catalytic activity of coated monoliths was evaluated towards MSR in a tubular reactor of AISI 310 (40 mm ID) placed in an electric oven, which provided sufficient heat to vaporize water. The entire plant was set to provide 3 kW of energy. The micro-reactor temperatures were measured by two K-type thermocouples located, respectively, at the inlet and outlet of the coated monolith. Before starting catalytic tests, the structured catalysts were reduced *in situ* sending a flow of 100 Nml min<sup>-1</sup> of H<sub>2</sub> at 200 °C for 1 h. The catalytic tests were performed over a temperature range of 550-850 °C, at different steam-to-carbon molar ratios (S/C: 3-3.2) and weight hourly space velocities (WHSV 750-3000 Nl h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). Mass flow controllers (Brooks Instrument Smart Mass Flow) were used to measure and control the flow of gaseous reactants. The gas stream composition at the reactor outlet is monitored by an ABB gas analyzer (NDIR module Uras 14 for CO/CO<sub>2</sub>/CH<sub>4</sub>, paramagnetic module Magnos 106 for O<sub>2</sub> and H<sub>2</sub>; water removed prior to entering the analyzer in a condenser at 3 °C). For all catalytic tests, measurements were repeated at least three times to assure their reproducibility and to check any possible aging phenomena on the structured catalysts.

The investigated catalysts were compared on the basis of CH<sub>4</sub> conversion, H<sub>2</sub> production, CO selectivity and H<sub>2</sub>/CO molar ratio. The CH<sub>4</sub> conversion is calculated to determine the amount of inlet CH<sub>4</sub> that has reacted and converted to products (Equation 3). This value is based on the total dry outlet flow rate (F<sub>out,dry</sub>), the inlet CH<sub>4</sub> flow rate (CH<sub>4,inlet</sub>) and the CH<sub>4</sub> concentration in the product mixture (CH<sub>4,conc</sub>).

$$CH_4 \text{ conversion} = \left[ 1 - \frac{\left( \frac{CH_{4,conc} \times F_{out,dry}}{100} \right)}{CH_{4,inlet}} \right] \times 100 \quad (3)$$

The H<sub>2</sub> production is the H<sub>2</sub> concentration in the product mixture (H<sub>2,conc</sub>). The H<sub>2</sub> selectivity (Equation 4) is based on the molar volume of gas mixture (assuming it is an ideal gas mixture) and the CH<sub>4</sub> and H<sub>2</sub> outlet flowrates (CH<sub>4,outlet</sub> and H<sub>2,outlet</sub>, respectively).

$$H_2 \text{ Selectivity} = \left[ \frac{H_{2outlet}}{\left( \left( \frac{CH_{4inlet}}{Molecular \ Volume} \right) - CH_{4outlet} \right)} \right] \times 100 \quad (4)$$

The CO selectivity (**Errore. L'origine riferimento non è stata trovata.**) is based on the molar volume of gas mixture (assuming it is an ideal gas mixture) and the CH<sub>4</sub> and CO outlet flowrates (CH<sub>4, outlet</sub> and CO<sub>outlet</sub>, respectively).

$$CO \text{ Selectivity} = \left[ \frac{CO_{outlet}}{\left( \left( \frac{CH_{4inlet}}{Molecular \ Volume} \right) - CH_{4outlet} \right)} \right] \times 100 \quad (5)$$

Finally, the molar ratio of H<sub>2</sub>/CO (Equation 6) is monitored to analyze the product in syngas concentration.

$$H_2/CO \text{ Ratio} = \frac{H_{2outlet}}{CO_{outlet}} \quad (6)$$

#### 2.4. Characterization on the best-selected catalyst

The specific surface area, textural properties of powder and structured samples were determined by N<sub>2</sub> physisorption at −196 °C using an ASAP 2020 instrument from Micromeritics. Prior to analysis, about 100 mg of each sample was outgassed overnight at 150 °C under high vacuum. The specific surface areas (S<sub>BET</sub>) were determined by Brunauer-Emmet-Teller (BET) method in the relative pressure range of 0.05 and 0.30.

By using the same apparatus, the chemisorption analysis was carried out, in order to evaluate the active metals dispersion on supports. H<sub>2</sub> saturation was first performed by flowing 20 Ncm<sup>3</sup> min<sup>−1</sup> of H<sub>2</sub> for 2 h at 350 °C, and at the end, a He flow rate of 20 Ncm<sup>3</sup> min<sup>−1</sup> for 1.5 h was fed to the apparatus increasing the temperature to 370 °C. Then, at room temperature, a mixture of 10% CO in He was injected in pulses of 500 NμL each, until the fulfillment of constant outlet peaks. The amount of adsorbed gas was determined as the difference between the total injected volume and the residual escaped one. The metal dispersion on the carrier surface was determined as follows:

$$D_{\%} = 100 \cdot S_f \cdot \frac{V_{ads} \cdot M_{me}}{V_g \cdot F_{me}} \quad (7)$$

considering the stoichiometric factor  $S_f$  is equal to 1 (i.e., each Ru atom adsorbed one CO molecule), the total volume of CO chemisorbed refers to the mass of the carrier used for the analysis in Ncm<sup>3</sup> g<sup>−1</sup> ( $V_{ads}$ ), the metal atomic weight  $M_{me}$  (101.07

g mol<sup>-1</sup> for Ru) and the total mass fraction of the metal on the catalyst (expressed as g<sub>me</sub> g<sup>-1</sup> of carrier), and that one gas g<sub>mole</sub>,  $V_g$ , occupies 22,414 cm<sup>3</sup> at normal conditions.

X-ray diffraction (XRD) patterns were collected using a Philips X-Pert MPD X-ray diffractometer equipped with Copper K $\alpha$  radiation at 40 kV and 30 mA to verify the effective composition of the samples and derive qualitative indications of the presence of comparatively large noble metals crystallite from its eventually visible peaks. All powder samples were scanned in the 2 $\theta$  range of 20-70° over 1h. The peaks were assigned according to the PCPFWIN database.

The surface morphology of the catalyst was examined by using Field-emission scanning electron microscopy FESEM (FESEM JEOL-JSM-6700F instrument). The elemental composition analysis was carried out by energy dispersive X-ray spectroscopy EDX (Oxford Instruments Inca EDX apparatus).

The geometrical properties of monoliths for square channel are calculated by [35–39]:

$$n = \frac{1}{(D+\delta_w)^2} \quad (8)$$

$$\varepsilon = D^2 \cdot n \quad (9)$$

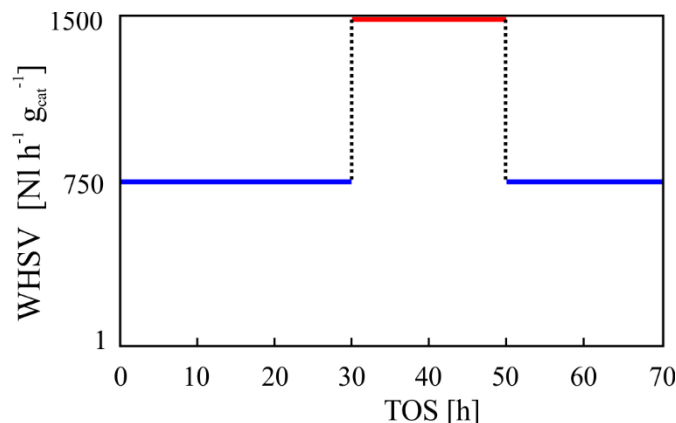
$$GSA = \frac{4(\sqrt{\varepsilon}-\varepsilon)}{\delta_w} \quad (10)$$

$$d_h = \frac{4 \cdot \varepsilon}{GSA} \quad (11)$$

where  $n$  is the cell density (N° cell·m<sup>-2</sup>),  $D$  inner length of the channel (m),  $\delta_w$  is the wall thickness (m),  $\varepsilon$  is the voidage for square channels,  $GSA$  is the geometric surface area (m<sup>2</sup> m<sup>-3</sup>) and  $d_h$  is the hydraulic diameter (m).

## 2.5. Stability measurements

Stability tests were performed over 70 h of time on stream (TOS) at 800 °C for the best-selected catalyst. The reactor was fed with a reactive mixture containing CH<sub>4</sub> and H<sub>2</sub>O with a S/C equal to 3 and WHSV equal to 750 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. At 30 h of TOS the WHSV was increased up to 1500 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. At 50 h of TOS the WHSV was reported to 750 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> till the end of the experiment (70 h of TOS), according to the thermal cycling shown in Figure 1.



**Fig. 1.** Thermal cycling for stability tests: WHSV vs WHSV at 800 °C and S/C of 3.

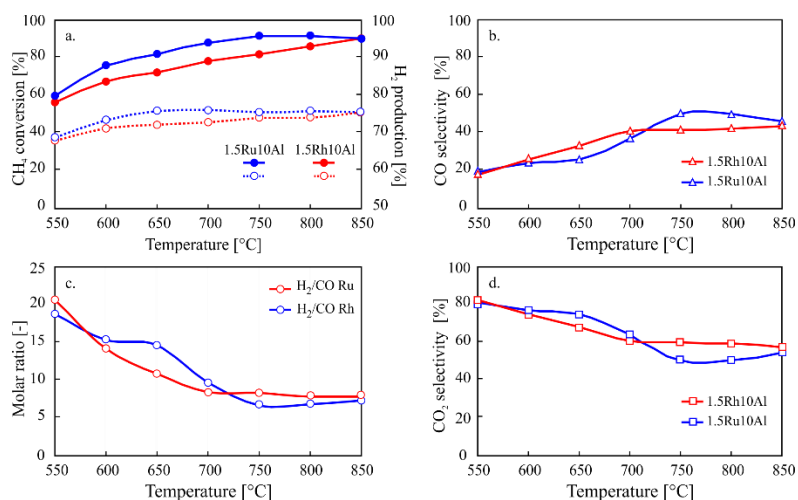
### 3. RESULTS AND DISCUSSION

#### 3.1. Ru/Rh metal on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier: metal-base catalysts comparison

In order to compare the catalytic performance of noble metals coated on monolith supports, Ru and Rh (active metal loading equal to 1.5 wt.%) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (10 wt.% on the bare cordierite monolith) were tested toward the MSR reaction. The experiments were carried out in the temperature range of 550 to 850 °C, S/C equal to 3.0, and WHSV of 750 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

As can be seen from Figure 2.a., both noble-metal-based catalysts do not reach complete methane conversion. However, the catalytic activity of the Ru-based one was found to be the most promising toward the MSR reaction in terms of CH<sub>4</sub> conversion, H<sub>2</sub> production, and CO selectivity. At temperatures higher than 750 °C, CH<sub>4</sub> conversion for 1.5Ru10Al catalyst remained slightly stable at 88.2 %, reaching the maximum conversion (91.0 %) at 800 °C, while for 1.5Rh10Al catalyst, CH<sub>4</sub> conversion increased for the entire temperature range studied achieving the maximum value of 87 % at 850 °C. On the other hand, H<sub>2</sub> produced for both catalysts was nearly the same, except at temperatures between 600-700 °C, where H<sub>2</sub> production was slightly higher for 1.5Ru10Al catalyst (Fig.2.a). As far as the selectivity of CO is concerned, both catalysts showed an increase in CO selectivity at temperatures between 550-700 °C. At temperatures above 700 °C, CO selectivity for 1.5Rh10Al catalyst remained stable at approximately 42 %, while for 1.5Ru10Al catalyst it continued to increase up to 750 °C, where it reached the maximum selectivity value of 50.25 % and then decreased due probably to the WGS reaction, which converts CO into CO<sub>2</sub> (Fig. 2.b). In fact, as shown in Figure 2.c, at temperatures between 725-850 °C, the H<sub>2</sub>/CO molar ratio was slightly higher for the Rh-based catalyst because of CO consumption (WGS reaction), which led

to a higher CO<sub>2</sub> selectivity compared to that obtained for the 1.5Ru10Al catalyst (Fig. 2.d). It is important to point out that the Ru-based catalyst produced a syngas richer in H<sub>2</sub> and selective to CO compared to the Rh-based catalyst one. For this reason, Ru was selected as the active metal phase for further investigations.



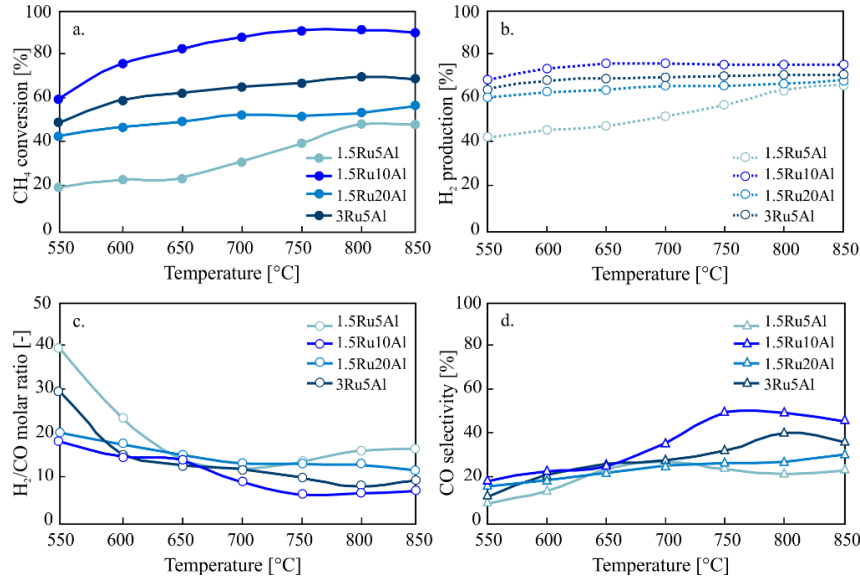
**Fig. 2.** MSR tests, performance comparison of monoliths 1.5% Ru and 1.5% Rh on 10%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at WHSV = 750 and S/C = 3. a) CH<sub>4</sub> conversion and H<sub>2</sub> production; b) CO selectivity; c) H<sub>2</sub>/CO molar ratio, and d) CO<sub>2</sub> selectivity.

### 3.2. Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst: loading comparison

The effect of catalyst loading on catalytic performance of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for MSR was studied by varying the amount of both the carrier and the active metal phase. Three different loads of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (5, 10, and 20 wt.%), corresponding to 3.20, 6.45, and 12.89 mg cm<sup>-2</sup>, respectively, were studied. Ru, as the noble metal phase, was loaded on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with two different percentages of active phase (1.5 and 3.0 wt.%, respectively) corresponding to a catalyst mass loading of 3.20 mg cm<sup>-2</sup>. All experiments were carried out in the temperature range of 550 to 850 °C, with fixed S/C molar ratio of 3.0 and volumetric flow equal to 32.65 NL h<sup>-1</sup>.

Fig. 3 (a-d) shows the effect of the carrier and active phase loading on the catalytic performance of the various catalytic monoliths. The results pointed out that the best catalytic performance was obtained with a load of 6.45 mg cm<sup>-2</sup> (corresponding to 10 wt.% of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 1.5 wt.% of Ru, sample 1.5Ru10Al), where the maximum CH<sub>4</sub> conversion achieved was 91 % at 800 °C (Fig. 3.a). On the other hand, H<sub>2</sub> concentration was quite stable for all catalyst at temperatures from 650 to 850 °C, with a H<sub>2</sub> production higher than 60 %, except for 1.5Ru5Al catalyst (Fig. 3.b), where the highest concentration of H<sub>2</sub> reached was 43.22 %. Analyzing the selectivity of CO and the H<sub>2</sub>/CO molar ratio (Fig. 3.c and 3.d), the highest concentration in dry reformat of CO was obtained for 1.5Ru10Al catalyst over the

entire temperature range studied. Interestingly, for the catalysts with mass loading of  $3.2 \text{ mg cm}^{-2}$  (corresponding to 5 wt. % of  $\text{Al}_2\text{O}_3$  on the bare monolith), the catalytic performance was significantly improved with increasing metal loading (from 1.5 to 3 wt.%). In fact, the maximum  $\text{CH}_4$  conversions reached at  $800^\circ\text{C}$  for 1.5Ru5Al and 3Ru5Al catalysts were 48.19 % and 69.24 %, respectively. Thus, the 3Ru5Al catalyst showed the second highest production of  $\text{H}_2$  and CO selectivity after the 1.5Ru10Al one. It is also important to note that all catalysts studied showed similar CO selectivity (23.37–27.08 %) at  $650^\circ\text{C}$ . Comparing with the results obtained by Amjad et al. [21] for Ru/ $\text{Al}_2\text{O}_3$  catalyst powder, similar results were reached in terms of  $\text{CH}_4$  conversion,  $\text{H}_2$  production, and CO selectivity in the temperature range of  $550$  to  $650^\circ\text{C}$ . Thus, according to our previous work [39], it is possible to conclude that by increasing catalyst loading by more than  $10 \text{ mg cm}^{-2}$ , the catalytic performance towards the MSR reaction decreases. This result can be explained considering that an excess of  $\text{Al}_2\text{O}_3$  carrier, which leads to a thicker layer covering the monolith walls, could not participate in the catalytic reaction and may even decrease both the dispersion of the noble metal and the number of active sites. Besides, it is well known that higher catalyst loadings lead to higher coating thickness and, therefore, a higher intraparticle mass transfer resistance, worsening the overall catalyst performance [40–42]. In the following section, we highlight in depth the mass transfer effects on structured monolith catalyst.



**Fig. 3.** MSR tests, performance comparison at WHSV = 750 and 3 S/C = 3 of Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  monoliths with different catalyst loadings: a)  $\text{CH}_4$  conversion; b)  $\text{H}_2$  production; c)  $\text{H}_2/\text{CO}$  molar ratio; d) CO selectivity.

### 3.4. Mass transfer effects on Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structured monolith catalyst

It is well known that the performance of a catalytic monolith involves a combination of reaction and transport processes, where the reactants and products undergo a series of steps over the catalyst, including: 1. diffusion of the reactants from the bulk gas phase to the external surface of the structured catalyst (external or inter-phase diffusion); 2. diffusion of the reactants into the catalyst pores to the active sites (internal or intra-phase diffusion); 3. adsorption of the reactants onto active sites; 4. reaction at specific active sites on the catalyst surface; 5. desorption of products from catalyst sites; 6. diffusion of the products through the catalyst pores (internal or intra-phase diffusion) and 7. diffusion of the products across the boundary layer surrounding the structured catalyst (external or inter-phase diffusion) [43–45].

According to the literature, three main regimes of catalytic rate control can exist in a coated monolith: (i) external/inter-phase diffusion regime (steps 1 and 7); (ii) internal/intra-phase diffusion regime (steps 2 and 6); and kinetic regime (steps 2 and 6) of the catalyst performance. Joshi et al. [46] developed a low-dimensional (LD) model to analyze catalytic reactions in washcoated monolith with channels of arbitrary shape. The LD model was derived directly by averaging the governing equations and using the concept of internal and external mass transfer coefficients, which were expressed in terms of three concentrations and two temperature modes and include washcoat diffusional effects without using the concept of effectiveness factor. Moreover, a practical criterion was developed to determine the transition between various controlling regimes in terms of resistances or concentration ratios [47]. We used this criterion to quantify the relative importance of reaction, pore diffusion, and external mass transfer processes in a coated monolith by SCS. Firstly, we defined the characteristic length scales for transverse diffusion associated within gas phase ( $R_{\Omega,e}$ ) and catalytic layer ( $R_{\Omega,i}$ ) in a monolith of square channel and circular diameter with a coated layer for the case of first order reaction. Then, we determined the external mass transfer coefficient ( $k_{m,e}$ ) between the bulk of gas phase and the fluid-catalytic layer interface as [48]:

$$k_{m,e} = \frac{Sh_e \cdot D_{CH_4-mix}}{4 \cdot R_{\Omega,e}} \quad (12)$$

and the internal mass transfer coefficient ( $k_{m,i}$ ) between the gas-catalytic layer interface and bulk of catalytic layer as:

$$k_{m,i} = \frac{Sh_i \cdot D_e}{R_{\Omega,i}} \quad (13)$$

where  $D_f$  is the molecular diffusivity of the reactant in gas phase ( $m^2 s^{-1}$ ),  $D_e$  is the effective diffusivity of CH<sub>4</sub> within coated layer ( $m^2 s^{-1}$ ),  $Sh_e$  and  $Sh_i$  are the external and internal Sherwood numbers, respectively. To determine  $Sh_e$  we considered the approximation proposed by Balakotaiah and West [49] used for any arbitrary geometry:

$$Sh_e = Sh_{e,\infty} + \frac{2.8}{Sc^{\frac{1}{6}}} \sqrt{P} \quad (14)$$

where  $Sh_{e,\infty}$  is the asymptotic external Sherwood number ( $Sh_{e,\infty} = 2.98$  for square channel),  $Sc$  is the Schmidt number, and  $P$  is the transverse Peclet number calculated as [50, 51]:

$$P = \frac{R_{\Omega,e}^2 \cdot u}{L \cdot D_{CH_4-mix}} \quad (15)$$

To estimate  $Sh_i$  we used the correlation proposed by Balakotaiah et al. [52]:

$$Sh_i = Sh_{i,\infty} + \frac{\Lambda \phi^2}{1 + \Lambda \phi} \quad (16)$$

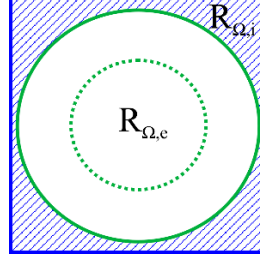
where  $Sh_{i,\infty}$  is the asymptotic internal Sherwood number,  $\phi$  is the Thiele modulus and  $\Lambda$  is a constant that depends on the coated layer geometric and kinetic parameter [48]. Table 2 shows the effective diffusion lengths, asymptotic external and internal Sherwood numbers and  $\Lambda$  for the channel shape and flow area under consideration. Thus, considering the following assumptions: 1. laminar and fully developed flow, 2. the hydraulic diameter of the channel much smaller than the length of cordierite monolith 3. isothermal conditions, and 4. first order kinetic; we expressed the overall resistance for mass transfer in a coated monolith by SCS according to Balakotaiah et al. [47] as:

$$R_t = R_e + R_i + R_r \quad (17)$$

$$\text{a. } R_e = \frac{4 \cdot R_{\Omega,e}}{Sh_e \cdot D_{CH_4-mix}} \quad \text{b. } R_i = \frac{R_{\Omega,i}}{Sh_i \cdot D_e} \quad \text{c. } R_r = \frac{1}{k_r \cdot R_{\Omega,i}} \quad (18)$$

with  $R_e$  resistance for external mass transfer ( $s \cdot m^{-1}$ ),  $R_i$  resistance for internal mass transfer ( $s \cdot m^{-1}$ ),  $R_r$  resistance for MSR reaction ( $s \cdot m^{-1}$ ), and  $R_t$  overall resistance for MSR process ( $s \cdot m^{-1}$ ).





**Fig. 4.** Definition of the characteristic length scales for transverse diffusion associated within gas phase ( $R_{\Omega,e}$ ) and catalytic layer ( $R_{\Omega,i}$ ) in a monolith of square channel and circular diameter with a coated layer.

To characterize the flow and the reactions the following five characteristic times are used [49, 53, 54]:

$$t_c = \frac{L}{u} \quad t_z = \frac{L_m^2}{D_{CH_4-mix}} \quad t_d^e = \frac{R_{\Omega,e}^2}{D_{CH_4-mix}} \quad t_d^i = \frac{\delta_c^2}{D_e} \quad t_r = \frac{C_{CH_4,in}}{r_{CH_4} \cdot \rho_c} \quad (19)$$

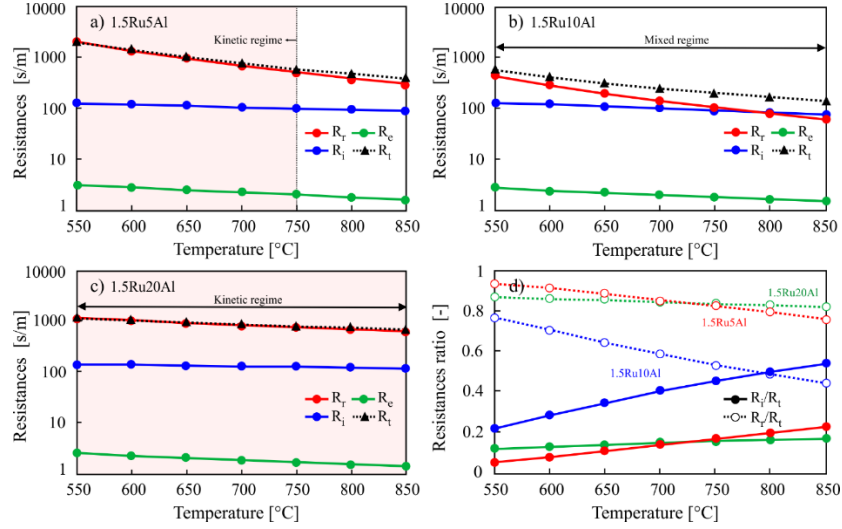
where  $t_c$  is the convection (or residence) time,  $t_z$  is the longitudinal diffusion time for the flow area,  $t_d^e$  is the transverse diffusion time for the flow area,  $t_d^i$  is the transverse diffusion time for the coated area, and  $t_r$  is the reaction time.

Catalyst	$R_{\Omega,e}$ [mm]	$R_{\Omega,i}$ [mm]	$Sh_{e,\infty}$	$Sh_{i,\infty}$	$\Lambda$
1.5Ru5Al	0.45	0.188	2.98	1.836	1.2
3Ru5Al	0.4508	0.1865	2.98	1.836	1.2
1.5Ru10Al	0.435	0.225	2.98	1.836	1.2
1.5Ru20Al	0.4	0.3182	2.98	2.533	0.73

**Table 2.** Effective diffusion lengths, asymptotic external and internal Sherwood numbers and  $\Lambda$  for square channel shape and circular flow area for the different catalyst studied.

In fig. 5 (a-d) we show the effect of  $\gamma\text{-Al}_2\text{O}_3$  amount on the controlling regimes towards MSR reaction on the prepared coated monolith catalysts. For all the catalysts studied, the resistances to mass transfer (inter/intra-phase diffusion) are much less temperature sensitive, since the diffusivities of reacting species in the gas phase ( $D_{CH_4-mix}$ ) and in the coated layer ( $D_e$ ) are much weaker functions of temperature in comparison to the reaction resistance, which is strongly dependent on Arrhenius equation. Thus, the interphase and intraparticle mass transfer rates increase only slightly with temperature. Therefore, as the catalyst temperature is

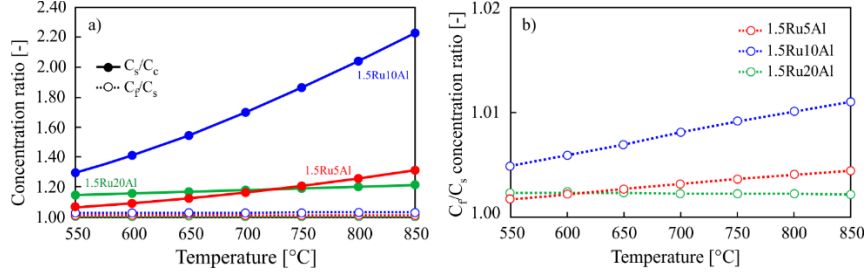
increased, the reaction rate increases exponentially, the reaction resistance becomes less dominant and the mass transfer resistances become important.



**Fig. 5.** Definition of the characteristic length scales for transverse diffusion associated within gas phase ( $R_{Q,e}$ ) and catalytic layer ( $R_{Q,i}$ ) in a monolith of square channel and circular diameter with different coating: a) 1.5Ru5Al; b) 1.5Ru10Al; c) 1.5Ru20Al; d) resistance ratios for all catalysts loading.

When comparing the effect of  $\gamma\text{-Al}_2\text{O}_3$  amount on the controlling regimes in catalytic monoliths, the 1.5Ru5Al monolith operates in a kinetic regime at temperatures lower than 750 °C (Fig.5.a). By increasing the  $\gamma\text{-Al}_2\text{O}_3$  loading to 20 wt.% (1.5Ru20Al catalyst), the process is completely controlled by the reaction for the entire temperature range studied (Fig.5.c). As a result, a nearly uniform concentration profile prevails in the transverse direction of the structure (fig 6). Thus, when the catalytic performance of MSR reaction is solely governed by the reaction kinetics, the total resistance ( $R_t$ ) is practically equal to the reaction resistance and the  $R_r/R_t$  ratio is greater than 0.8 (Fig 5.d). Besides, as expected, when the monolith operates in a kinetic regime, the characteristic times for the MSR reaction are much larger than that for the external and internal mass transfer diffusion (see Table S.I X). On the other hand, for the 1.5Ru10Al catalyst (10 wt.% of alumina,  $6.45 \text{ mg cm}^{-2}$ ), the monolith operates in a mixed regime for all temperature range studied, in which both the kinetic and the intraparticle diffusion co-exist (fig.5.a), with both  $R_r/R_t$  and  $R_i/R_t$  lower than 0.8. By observing the catalytic performance for the different loading of  $\gamma\text{-Al}_2\text{O}_3$  (Fig. 3), it is worth noting that for the 1.5Ru20Al catalyst, the conversion of  $\text{CH}_4$  increases slightly with temperature, being practically steady for the temperature range under consideration. This effect explains why the reaction resistance is practically independent with temperature.

On the contrary, for the 1.5Ru10Al catalyst, CH<sub>4</sub> conversion increases more rapidly with temperature up to 750 °C, and then remains slightly stable.

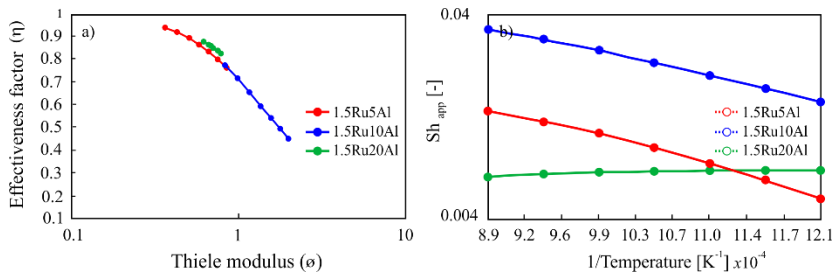


**Fig. 6.** Concentration ratios for the various catalysts tested.

To gain insight into the catalyst activity by varying the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content, we evaluated the Thiele modulus ( $\phi$ ) and the effectiveness factor ( $\eta$ ) for a first-order kinetics reaction, according to the following equations [47, 48]:

$$\phi = \sqrt{\frac{k_r \cdot R_{\Omega,i}^2}{D_e}} \quad \eta = \frac{1}{1 + \frac{\phi^2}{Sh_i}} \quad (20)$$

where  $k_r$  is the observed first-order reaction rate constant (s<sup>-1</sup>),  $R_{\Omega,i}$  the effective transverse diffusion length in the coated catalyst layer for the internal resistance (m),  $D_e$  is the effective diffusivity of CH<sub>4</sub> (m<sup>2</sup> s<sup>-1</sup>), and  $Sh_i$  is the internal Sherwood number. All the correlations and physical parameters used for the calculations of  $\phi$  and  $\eta$  are available in the Appendix. Fig.7 shows the effectiveness factor as a function of Thiele modulus for the different catalyst loadings. As expected, the effectiveness factor for the case of slow reaction  $\phi \ll 1$  tends to unit. In particular, the 1.5Ru20Al catalyst showed a variation of  $\phi$  much less sensitive to temperature ( $0.82 < \phi < 0.87$ ) than the other catalyst loadings, indicating that the process is rate-limited and the reaction rate is controlled by the intrinsic kinetics.



**Fig. 7.** Effectiveness factor (a) and apparent Sherwood number (b) for the various coated monoliths.

Additionally, we plot the experimentally observable overall Sherwood number ( $Sh_{app}$ ) calculated using Eqn. 21 as a function of reciprocal of temperature on a logarithmic scale (Fig. 7b). The theoretical upper limit for  $Sh_{app}$  ( $Sh_{e,\infty}$ ) is 2.98 for the channel shape under consideration (square channel with circular flow area) [50, 51].

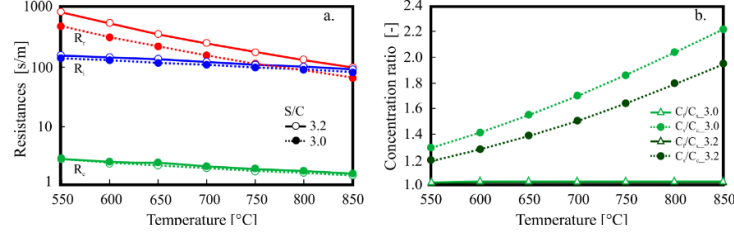
$$\frac{1}{Sh_{app}} = \frac{1}{Sh_e} + \frac{\mu\lambda}{4} \cdot \frac{1}{Sh_i} + \frac{\mu\lambda}{4\phi^2} \quad (21)$$

$$\mu = \frac{R_{\Omega,i}}{R_{\Omega,e}} \quad \lambda = \frac{D_f}{D_e} \quad (22)$$

It is evident from the results that the experimental conditions used lead to rather low values of  $Sh$ . Bennett et al. [55] reported a value of  $Sh_{app}$  as small as 0.05, which was attributed to the low activation energies and pre-exponential factors obtained for the catalytic oxidation of propane. Similar results were obtained by Joshi et al. [56] for the case of hydrogen oxidation on Pt, which presents a very low intrinsic activation energy ( $\sim 9 \text{ kJ mol}^{-1}$ ), obtaining experimental Sherwood numbers ( $Sh_{app}$ ) less than 0.55. In our study, the apparent activation energies obtained for the MSR reaction were determined from the conversion data ( $X_{CH_4} < 5 \%$ ) for the different catalyst loads ( $Ea_{app} \approx 50 \text{ kJ mol}^{-1}$ ). These values are low compared to other activation energies on supported Ru catalyst for MSR reaction [57, 58]. As shown in Fig. 7b, low  $Sh_{app}$  values (below 0.035) are obtained for the three catalysts studied, especially for 1.5Ru20Al catalyst.

On the other hand, it is interesting to note that the ratios of reactant diffusivities in the gas phase and the coated layer ( $\mu$ ) obtained in our study are greater than 225. Joshi et al. [48] studied the variation of  $Sh_{app}$  for the different controlling regimes by varying the values of  $\mu$  for circular channel with circular flow area. They obtained that for values of diffusivity ratios higher than 200, the  $Sh_{app}$  for  $\phi \ll 1$  (slow reaction) are much lower than 0.1 ( $\sim 10^{-2}$ - $10^{-3}$ ), as obtained in this study.

To study the effect of WHSV and S/C molar ratio on the controlling regimes in a coated monolith by SCS, we selected the 1.5Ru10Al catalyst according to the best results obtained in terms of  $CH_4$  conversion,  $H_2$  production, and CO selectivity. The 1.5Ru10Al catalyst was studied at space velocities of 750, 1,500, and 3,000  $NL \text{ h}^{-1} \text{ g}_{cat}^{-1}$ , calculated on metal basis, and S/C molar ratio of 3 and 3.2 respectively. As visible in Fig. 8, as the S/C molar ratio increases, both the mass transfer resistances and the reaction resistance increase. In particular,  $R_r$  for the S/C molar ratio of 3.2 is about 1.5 times higher than that obtained at S/C 3 for the entire temperature range studied. Since the catalytic performance decreased as the S/C molar ratio increased (Fig. A1), lower rate constants ( $k_r^{obs}$ ) were obtained for S/C equal to 3.2, thus increasing the reaction resistance. Since a higher bulk reaction controlling is obtained either by increasing the S/C molar ratio as the WHSV, a concentration profile closer to the unit exists in the transverse direction of the monolith (Fig. 8b).



**Fig. 8.** Resistances (a) and concentration ratios for different S/C values for the 1.5Ru10Al coated monolith.

### 3.5. Heat transfer effects on Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structured monolith catalyst

For heterogeneous catalytic processes, heat management in chemical reactions is a very important aspect for both reactor design and overall performance of the process. In addition to mass transfer effects, heat transfer effects can also occur in heterogeneous catalysis for reactions with a significant heat of reaction, either exothermal or endothermal such as combustion or steam reforming [45, 59, 60]. External temperature gradients between the bulk of the fluid phase and the surface of the catalytic layer are originated from the reaction enthalpy associated with surface reaction. The external temperature difference can be large even when mass transfer limitations are negligible, which disguises the actual reaction kinetics occurring at surface temperature ( $T_s$ ) and not at the bulk of the fluid phase temperature ( $T_b$ ). The surface temperature can be determined by the heat balance at steady state conditions, assuming that the outer surface of the catalyst layer is uniformly available for the reactants. In this way, each section of the outer surface behaves kinetically in the same way as all other parts, thus the steady-state analysis of that system is essentially one-dimensional [45, 59]. For more details of the heat balance go to the supplementary information section. We report the final expression of the heat balance using the Chilton-Colburn analogies between mass and heat transfer:

$$(T_b - T_s) = \left( \frac{\Delta H_r \cdot C_b}{\rho_f \cdot c_{p,f}} \right) \cdot Le^{-2/3} \cdot Ca \quad (23)$$

$$Le = \frac{Sc}{Pr} ; \quad Ca = \frac{c_b - c_s}{c_b} \quad (24)$$

where  $T_b, T_s$  is the temperature in the bulk of the gas phase and surface of the catalyst layer (K) respectively,  $\Delta H_r$  is the heat of MSR reaction (J mol<sup>-1</sup>),  $C_b$  is the concentration in the bulk of the gas phase (mol m<sup>-3</sup>),  $\rho_f$  is the density of the gas phase (Kg m<sup>-3</sup>),  $c_{p,f}$  is the heat capacity of the gas phase (J Kg<sup>-1</sup> K<sup>-1</sup>),  $Le$  is the fluid Lewis number,  $Pr$  is the Prandtl number and  $Ca$  is the Carberry number. Thus, by dividing Equation 23 by  $T_b$ , it is possible to obtain the dimensionless external Prater

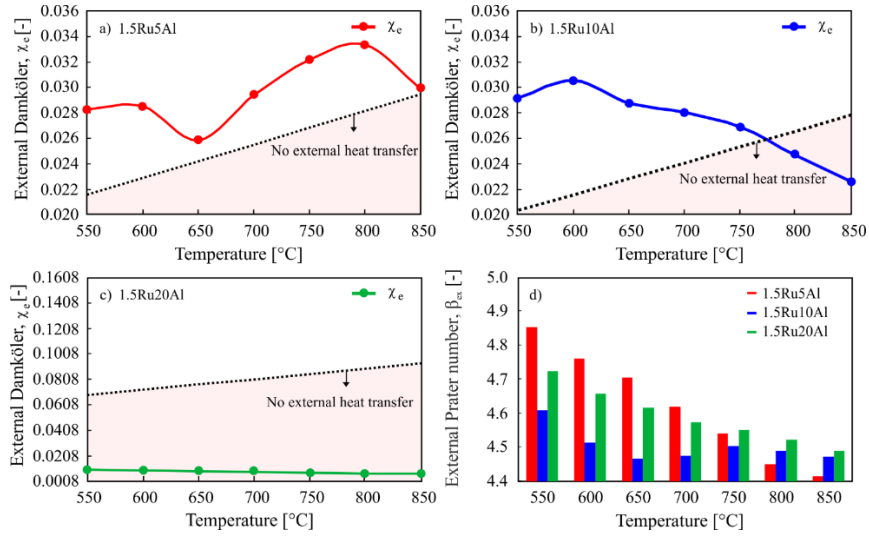
number which represents the ratio of the maximum heat consumption and heat transfer rates:

$$\beta_{ext} = \frac{\Delta T_{ad}}{T_b} \cdot Le^{-2/3} = \left( \frac{\Delta H_r \cdot C_b}{\rho_f \cdot c_{p,f}} \right) \cdot \frac{1}{T_b} \cdot Le^{-2/3} \quad (25)$$

The interphase heat transfer limitations can be evaluated using the criterion derived by Mears [61] (Eq. 26) with the perturbation approach, in which the heat transfer resistance of the fluid phase is assumed to be lumped at the surface. We use this criterion to estimate the external heat transfer effects by varying the alumina content in the monolithic catalyst:

$$\chi = \frac{(\Delta H \cdot R^{obs, R\Omega e})}{h_e \cdot T_b} < \frac{0.15}{\gamma_b}; \quad \gamma_b = \frac{E_{act}}{R_g \cdot T_b} \quad (26)$$

where  $R^{obs}$  is the observed reaction rate ( $\text{mol m}^3 \text{s}^{-1}$ ),  $h_e$  is the heat transfer coefficient associated for the gas phase ( $\text{W m}^{-2} \text{K}^{-1}$ ),  $R_g$  is the gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $E_{act}$  is the apparent activation energy of the reaction ( $\text{J mol}^{-1}$ ),  $\chi$  is the Damkholer for interphase heat transport and  $\gamma_b$  is the Arrhenius number evaluated at the bulk of the gas phase.



**Fig. 9.** External Damköhler numbers in a monolith of square channel and circular diameter with different coating: a) 1.5Ru5Al; b) 1.5Ru10Al; c) 1.5Ru20Al. External Prater number for the various catalysts loading (d).

As observed in Fig. 9, for the 1.5Ru5Al2O3 catalyst, external heat transfer limitations are presented for the complete temperature range studied, while for the 1.5Ru10Al catalyst the thermal effects are important a temperature below 725°C. On the other hand, not interphase heat transfer limitations are observed for the higher catalyst loading. It is important to note that for the lower alumina content the temperature difference between the bulk of the gas phase and the surface of the catalytic layer increases considerably as the inlet gas temperature increases from 650-800 °C, and then start to decrease probably as mentioned above, in this temperature range initiates the WGS reaction which is exothermic and leads to an increase in the  $T_s$ . For catalysts with 10 and 20 wt.% of alumina, the  $\Delta T$  is practically constant as the temperature of the reactant gas increases, approximately 70 and 25 K respectively. It is also important to point out that the temperature difference between bulk and outer catalytic layer surface is directly proportional to the heat of MSR reaction per mol of diffusing reactant and the fractional drop in concentration between the bulk of the gas phase and the surface of the catalyst layer (see eq. 23). Thus, the quotient of the heat consumed by complete reaction of unit volume of reacting gas mixture ( $\Delta H_r \cdot C_b$ ) and the volumetric heat capacity of the reacting mixture ( $\rho_f \cdot c_{p,f}$ ) gives the temperature rise equivalent to complete adiabatic conversion of the reacting mixture when  $C_s$  is zero. The eq. 23 also shows that heat transfer limitation and  $\Delta T$  may be significant if  $\Delta H_r$  values are large, even when concentration gradients are small as those obtained in section 3.4 for all the alumina loading studied. Since the MSR reaction is highly endothermic, the temperature of the catalyst surface will be less than in the bulk fluid phase, and the observed rate will be less than that corresponding to the bulk-fluid temperature. In addition to the interphase heat transfer limitations, a large number of highly exothermic and endothermic catalytic reactions are accompanied by internal thermal effects, particularly for relatively fast intrinsic kinetics. Anderson in 1963 [62] applied the perturbation approach to derive a criterion for the lack of importance of temperature gradients in catalyst particles. The reaction is assumed to follow Arrhenius temperature dependence and this criterion is valid regardless of whether there are diffusion limitations in the particle or not. Thus, we use this criterion to evaluate the intraparticle heat transfer effects by varying the alumina content in the structured catalyst:

$$\frac{(\Delta H \cdot R^{obs} \cdot R_{\theta l}^2)}{\lambda_{cat} \cdot T_s} < \frac{0.75}{\gamma_s} \quad (27)$$

$$\psi = \frac{(\Delta H \cdot R^{obs} \cdot R_{\theta l}^2)}{\lambda_{cat} \cdot T_s}; \quad \gamma_s = \frac{E_{act}}{R_g \cdot T_s} \quad (28)$$

where  $\lambda_{cat}$  is the thermal conductivity of the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst (W m<sup>-1</sup> K<sup>-1</sup>),  $\psi$  is the Damkohler for intraparticle heat transport and  $\gamma_s$  is the Arrhenius number evaluated at the surface of the gas phase. As observed from the Fig. 10 (a-c), for all the catalyst loading studied  $\psi \ll \frac{0.75}{\gamma_s}$  indicating that the absence of intraparticle

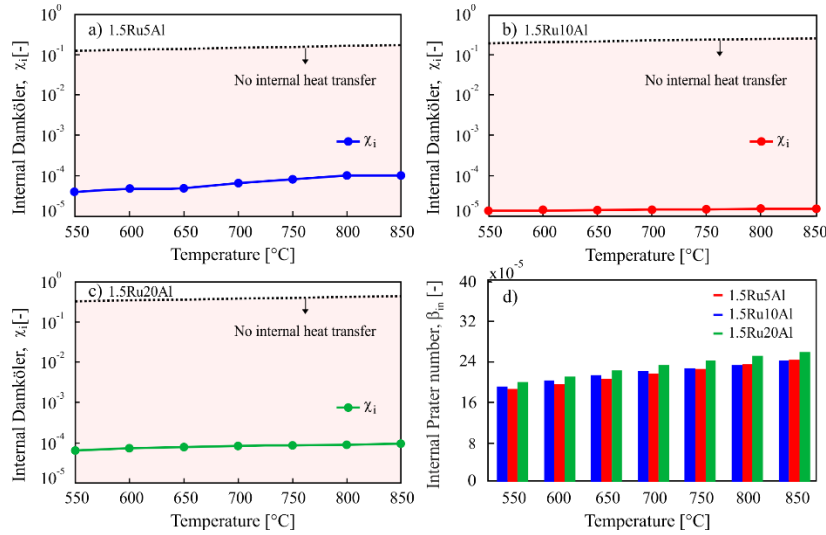
heat transfer. This can also be observed by studying the temperature gradients within the catalytic layer using the relationship originally derived by Damköhler in 1943 [63], which is valid for all the kinetics and applies to all the particle geometries assuming that  $T_s$  and  $C_s$  are uniform over the entire boundary surface [45]:

$$(T_s - T_{b,c}) = (\Delta H_r) \cdot \frac{D_e}{\lambda_e} \cdot (C_s - C_{b,c}) \quad (29)$$

where  $T_{b,c}$  is the temperature in the bulk of the catalyst layer (K),  $C_{b,c}$  is the concentration within the catalyst layer and  $\lambda_e$  is the effective thermal conductivity. It is worth noting the largest possible temperature difference into the catalyst layer is attained when the concentrations within the bulk of the catalyst layer becomes zero, hence we can refer the maximum temperature difference ( $\Delta T_{max}$ ) to the surface temperature using the dimensionless internal Prater number ( $\beta_{in}$ ) by [45, 59]:

$$\beta_{in} = \frac{\Delta T_{max}}{T_s} = \frac{(\Delta H_r) \cdot C_s}{T_s} \cdot \frac{D_e}{\lambda_e} \quad (30)$$

As shown in Fig. 10 d, all  $\beta_{in}$  values are much smaller than one, indicating the absence of temperature gradients within the catalytic layer, confirming in this way the results obtained by using the Anderson criterion.



**Fig. 10.** Internal Damköhler numbers in a monolith of square channel and circular diameter with different coating: a) 1.5Ru5Al; b) 1.5Ru10Al; c) 1.5Ru20Al. Internal Prater number for the various catalysts loading (d).



In the following section, we will discuss the results obtained of the physico-chemical characterization on the best catalyst-selected.

### 3.6 Characterization of powdered catalyst and coated structured supports.

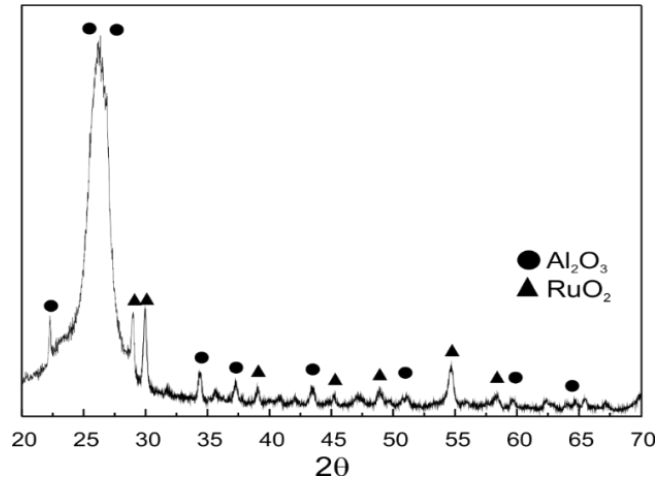
Table 3 shows the specific surface area ( $S_{BET}$ ) of powder samples, bare and coated monoliths. Comparing with the pure powder of  $\gamma$ - $Al_2O_3$ , the  $S_{BET}$  of 1.5 wt.% Ru/ $\gamma$ - $Al_2O_3$  powder catalyst was decreased by 82.6%, to  $191.5 \text{ m}^2 \text{ g}^{-1}$ . Instead, considering the practically zero  $S_{BET}$  of the bare monolith, As expected, the deposition of  $\gamma$ - $Al_2O_3$  on the monolith, as carrier of Ru (the active metal) notably increased the  $S_{BET}$  of the bare monolith.

Catalyst	$S_{BET} [\text{m}^2 \text{ g}^{-1}]$
$\gamma$ - $Al_2O_3$ powder	231.7 [39]
Ru/ $\gamma$ - $Al_2O_3$ powder	191.5 [21]
1.5 wt. % Ru/ $\gamma$ - $Al_2O_3$ on cordierite monolith	23.8
Bare cordierite monolith	0.009

**Table 3.** Specific surface area values of different types of catalysts.

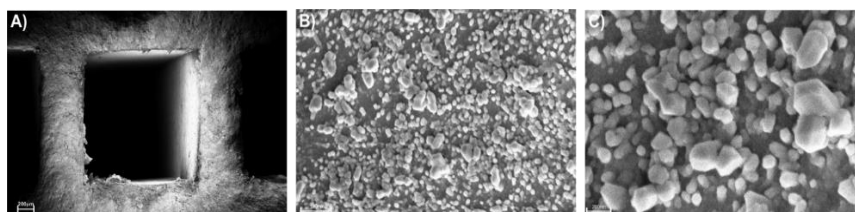
Ru metal dispersion and crystallite size obtained from  $H_2$  chemisorption were 5.3% and 25 nm, respectively. Similar results were obtained in our previous work in terms of crystal size [33], while a greater dispersion of Ru is obtained when the catalyst is prepared in a single step by SCS.

Fig. 11 shows the XRD diffraction patterns of the 1.5 wt.% Ru/ $\gamma$ - $Al_2O_3$  catalyst, compared with the reference patterns of  $\gamma$ - $Al_2O_3$  and  $RuO_2$ . The diffractogram shows the peaks related to the Ru in its oxidized form ( $RuO_2$  JCPDS database, ref. 00-002-1365) and the  $\gamma$ - $Al_2O_3$  in its amorphous structure (JCPDS database, ref. 00-001-1243).



**Fig. 11.** XRD patterns of 1.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O catalyst, with the reference peaks of RuO<sub>2</sub> (JCPDS database, ref. 00-002-1365) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS database, ref. 00-001-1243).

Figure 12 shows FESEM images of the coated monolith. There is a good dispersion of the catalytic particles on the surface of the monolith. In particular, alumina particles on the surface of the monolith are well dispersed by providing sufficient specific surface area to host Ru. Furthermore, Ru particle size distribution on Al<sub>2</sub>O<sub>3</sub> particles seems to be wider. Table 4 shows the EDX analysis coupled with FESEM, giving evidence of the presence of Ru particles and alumina.



**Fig. 12.** FESEM images of 1.5% Ru on 10% alumina on 100 cpsi monolith at different magnifications. **A)** 100X, **B)** 50000 kX, **C)** 150000 kX.

Element	Weight %	Atomic %
O	53.45	68.56
Mg	1.09	0.92
Al	34.88	26.50
Si	5.54	2.58
Ru	7.04	1.44
Tot	100.00	100.00

**Table 4.** EDX analysis of the 100 cpsi monolith coated with 1.5% Ru on 10% alumina.

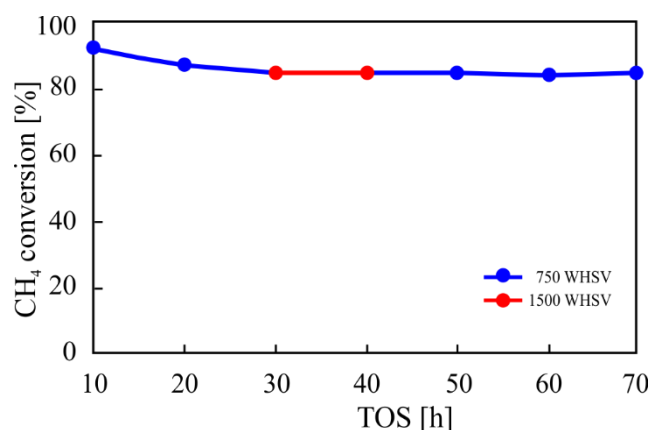
### 3.7 Ageing test on the best performing coated monolith.

After performing various experiments, the catalyst 1.5Ru10Al performed best in all types of test. The conversion remained higher than the others and it showed high productivity and higher CO selectivity at low WHSV for temperatures between 600-750°C and S/C 3. The most competitive catalyst with the same experimental conditions was Rh, but it was clearly seen that the difference in performance was almost more than 8%.

Furthermore, a new cordierite monolith was coated with the best catalyst, 1.5%Ru/10%Al<sub>2</sub>O<sub>3</sub>, and its catalytic performance was evaluated with respect to

time. Figure 13 shows methane conversion versus the time on stream (TOS), at two different WHSV. In the first 30 hrs, reaction conditions were fixed at 800 °C, WHSV = 750 and S/C = 3. Then, for the next 20 hrs, WHSV was increased to 1500, and finally reduced again to 750 (being T and S/C always constant at 800 °C and 3, respectively). Clearly, the coated monolith kept methane conversion almost constant at its starting value, independent of the variation of WHSV.

Thus, this test confirms that overall at the temperature of 800 °C, even when varying the WHSV, no significant difference is recorded in methane conversion, which remained stable throughout the time period.



**Fig. 13.** Stability test of the cordierite monolith coated with 1.5%Ru/10%Al<sub>2</sub>O<sub>3</sub> catalyst at 800 °C and S/C = 3. WHSV variable between 750 and 1500  $\text{Nl h}^{-1} \text{g}_{\text{cat}}^{-1}$ .

#### 4. CONCLUSION

In this study, the catalytic performance and mass/heat transfer effects were evaluated for Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst supported on ceramic cordierite monolith towards MSR reaction. All the catalysts were prepared in a single step by solution combustion synthesis coated on over monolith of square channel with 100 cpsi. By comparing the catalytic performance of Ru and Rh as active metal phase, the Ru-based catalyst was found to be more active towards MSR reaction, showing a syngas richer in H<sub>2</sub> for the entire temperature range studied. The best catalyst loading of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was 6.45  $\text{mg cm}^{-2}$ , where the excess of Al<sub>2</sub>O<sub>3</sub> carrier could only lead to a thicker layer and not participate in the catalytic reaction, leading to the catalyst working in an entirely kinetic regime. The temperature dependence on the external and internal diffusion regimes is much weaker compared to the reaction resistance, which is strongly dependent of the Arrhenius equation. External heat transfer limitations were presented at lower carrier content, while that low values of internal Prater numbers confirmed the absence of internal heat limitation. An

excellent stability of the 1.5% Ru on 10% Al<sub>2</sub>O<sub>3</sub> catalyst (1.5Ru10Al sample) was observed over 70 h of TOS for MSR process.

## 5. APPENDIX

In the following, a detailed explanation of fluid and catalyst layer properties determination, characteristic time analysis, external and internal mass transfer calculations and heat transfer investigation is reported.

### A.1 Estimation of fluid properties

Molecular weight ( $M_{mix}$ ), density ( $\rho_f$ ) and viscosity ( $\mu_f$ ) of gas mixture were calculated as:

$$M_{mix} = \sum_{i=1}^n y_i M_i \quad (S1)$$

$$\rho_f = \frac{P M_{mix}}{R_g T} \quad (S2)$$

$$\mu_f = \frac{\sum_{i=1}^n \mu_i y_i M_i^{1/2}}{\sum_{i=1}^n y_i M_i^{1/2}} \quad (S3)$$

where  $y_i$  is the mole fraction of the compound,  $M_i$  is the molecular weight of the compound (kg kmol<sup>-1</sup>),  $P$  is the pressure (kPa),  $T$  is the absolute temperature (K),  $R$  is the universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>) and  $\mu_i$  is the viscosity of a single component (kg m<sup>-1</sup> s<sup>-1</sup>).

Gas viscosity ( $\mu_i$ ,  $\mu$ P) of a single component was calculated as:

$$\mu_i = A + BT + CT^2 \quad (S4)$$

using the tabulated values of A, B, and C [64].

	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>
A	3.844	-36.826	27.758	23.811	11.811
B	0.40112	0.429	0.212	0.53944	0.49838
C	-0.00014303	-0.0000162	-0.0000328	-0.00015411	-0.0001085

**Table A1.** Values of A, B, and C used in eq. S.4.

The diffusivity of CH<sub>4</sub> in gas mixture ( $D_{CH_4-mix}$ , cm<sup>2</sup> s<sup>-1</sup>) was calculated from the binary diffusion of CH<sub>4</sub> and  $i$  gas species ( $D_{CH_4-i}$ ) by:

$$D_{CH_4-mix} = \frac{1 - y_{CH_4}}{\sum_{i=1, i \neq CH_4}^n \frac{y_i}{D_{CH_4-i}}} \quad (S5)$$

where  $D_{CH_4-i}$  was determined by Fuller equation (eq. S.6) [65], using tabulated values of  $v_i$  [66].

$$D_{CH_4-i} = \frac{10^{-3} T^{1.75} \left( \frac{1}{M_{CH_4}} + \frac{1}{M_i} \right)}{P \left( v_{CH_4}^{1/2} + v_i^{1/3} \right)^2} \quad (S6)$$

where  $v_i$  are tabulate in Table A2.

	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>
$v_i$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	24.4	12.7	7.1	18.9	26.9

**Table A2.** Values of  $v_i$  used in eq. S.6.

The effective diffusivity of methane ( $D_{CH_4,e}$ ) in the catalytic layer was calculated using the following equation [67, 68]:

$$D_{CH_4,e} = \frac{\varepsilon_c}{\tau_c} \cdot \left( \frac{1}{D_{CH_4-mix}} + \frac{1}{D_k} \right)^{-1} \quad (S7)$$

where  $\varepsilon_c$  is the coated layer porosity ( $\varepsilon_c = \rho_c \cdot V_{BJH}$ ) [69],  $\tau$  is the tortuosity factor ( $\tau = 2 - \varepsilon_c$ ) [70] and the Knudsen diffusion ( $D_k$ ) was determined by eq. S.8 [71]:

$$D_k = 9700 \cdot r_p \cdot \sqrt{\frac{T}{M_{CH_4}}} \quad (S8)$$

where  $\rho_c$  (kg m<sup>-3</sup>) is the bulk density of the catalyst (3500 kg m<sup>-3</sup>),  $V_{BJH}$  is the total pore volume (cm<sup>3</sup> g<sup>-1</sup>),  $r_p$  is the pore diameter (cm) and  $M_{CH_4}$  is the molecular weight of CH<sub>4</sub>.

The mass transfer coefficient of CH<sub>4</sub> ( $k_G$ , m s<sup>-1</sup>) was determined from the Sherwood number ( $Sh$ ) by:

$$k_G = \frac{Sh \cdot D_{CH_4-mix}}{d_h} \quad (S9)$$

where  $Sh$  is calculated from Reynold ( $Re$ ) and Schmidt ( $Sc$ ) numbers by Eqs. S.10, S.11 and S.12 [60, 72, 73].

$$Sh = 2.976 \cdot \left( 1 + 0.095 \cdot Re \cdot Sc \cdot \frac{d_h}{L_m} \right)^{0.45} \quad (S10)$$

$$Re = \frac{d_h \cdot u_0 \cdot \rho_f}{\mu_f} \quad (S11)$$

$$Sc = \frac{\mu_f}{\rho_f \cdot D_{CH_4-mix}} \quad (S12)$$

where  $d_h$  is the hydraulic diameter of the bare monolith (m),  $L_m$  is the monolith length (m),  $u_0$  is the inlet gas velocity at operative conditions ( $m\ s^{-1}$ ),  $\rho_f$  is the density of gas mixture ( $kg\ m^{-3}$ ),  $\mu_f$  is the viscosity of gas mixture ( $kg\ m^{-1}\ s^{-1}$ ) and  $D_{CH_4-mix}$  is the diffusivity of  $CH_4$  in gas phase ( $m^2\ s^{-1}$ ).

The inlet gas velocity at operative conditions  $u_0$  ( $m\ s^{-1}$ ) was calculated as:

$$u_o = \frac{F_{ch}}{A_{ch} \cdot \varepsilon} \cdot \frac{T}{T_{St}} \cdot \frac{P}{P_{St}} \quad (S13)$$

where  $F_{ch}$  is the total flow of the gas mixture for channel ( $m^3\ s^{-1}$ ),  $\varepsilon$  is the coated monolith voidage,  $A_{ch}$  is the frontal area of the bare monolith for square channel ( $m^2$ ),  $T_{St}$  (K) and  $P_{St}$  (Pa) are the standard temperature and pressure,  $T$  (K) and  $P$  (Pa) are the operative temperature and pressure.

The thermal conductivity of gas mixture ( $\lambda_{mix}$ ,  $W\ m^{-1}\ K^{-1}$ ) was calculated as:

$$\lambda_{mix} = \frac{\sum_{i=1}^n \lambda_i y_i M_i^{1/2}}{\sum_{i=1}^n y_i M_i^{1/2}} \quad (S14)$$

where  $\lambda_i$  is the thermal conductivity of a single component ( $W\ m^{-1}\ K^{-1}$ ) calculated as:

$$\lambda_i = A + BT + CT^2 \quad (S15)$$

using the tabulated values of A, B, and C [64].

	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>
A	-0.00935	0.00053	0.03951	0.00158	-0.01200
B	1.4028E-04	4.7093E-05	4.5918E-04	8.2511E-05	1.0208E-04
C	3.3180E-08	4.9551E-08	-6.4933E-08	-1.9081E-08	-2.2403E-08

**Table A3.** Values of A, B, and C used in eq. S.15.

The heat capacity of the gas mixture ( $Cp_f$ ,  $J\ mol^{-1}\ K^{-1}$ ) was calculated as:

$$Cp_f = \frac{\sum_{i=1}^n Cp_i y_i M_i^{1/2}}{\sum_{i=1}^n y_i M_i^{1/2}} \quad (S16)$$

where  $Cp_i$  is the heat capacity of a single component ( $J\ mol^{-1}\ K^{-1}$ ) calculated as [64]:

$$Cp_i = A + BT + CT^2 + DT^3 + ET^4 \quad (S17)$$

	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>
<b>A</b>	34.942	33.933	25.399	29.556	27.437
<b>B</b>	-3.9957E-02	-8.4186E-03	2.0178E-02	-6.5807E-03	4.2315E-02
<b>C</b>	1.9184E-04	2.9906E-08	-3.8549E-05	2.0130E-05	-1.9555E-05
<b>D</b>	-1.5303E-07	-1.7825E-08	3.188E-08	-1.2227E-08	3.9968E-09
<b>E</b>	3.9321E-11	3.6942E-12	-8.758E-12	2.2617E-12	-2.9872E-13

**Table A4.** Values of A, B, C, D, and E used in eq. S.17.

### A.2 Estimation of coated layer properties

Specific surface area ( $SA_{BET} = 23.79 \text{ m}^2 \cdot \text{g}^{-1}$ ) was determined from Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analytic methods for N<sub>2</sub> adsorption-desorption isotherms. Pore radius ( $r_p = 100 \text{ \AA}$ ) was given by  $2PV_{BJH}/SA_{BET}$  equation.

### A.3 Characteristic time analysis

The characteristic contact time, or residence time ( $t_c$ , s) is determined by [73]:

$$t_c = \frac{L_m}{u_o} \quad (\text{S18})$$

where  $L_m$  is the monolith length (m) and  $u_o$  is the inlet gas velocity at operative conditions ( $\text{m s}^{-1}$ ).

The transverse diffusion time for the flow area ( $t_d^e$ , s) is determined by [73]:

$$t_d^e = \frac{R_{\Omega e}^2}{D_{CH_4-mix}} \quad (\text{S19})$$

where  $R_{\Omega e}$  is the characteristic length scale for the fluid phase (m) and  $D_{CH_4-mix}$  is the diffusivity of CH<sub>4</sub> in gas phase ( $\text{m}^2 \text{ s}^{-1}$ ).

The transverse diffusion time for the coated area ( $t_d^i$ , s) is determined by [73]:

$$t_d^i = \frac{\delta_c^2}{D_{CH_4,e}} \quad (\text{S20})$$

where  $D_{CH_4,e}$  is the effective diffusivity of CH<sub>4</sub> in the coated layer ( $\text{m}^2 \text{ s}^{-1}$ ) and  $\delta_c$  is the coated layer thickness (m) calculated as [47]:

$$\delta_c = \frac{l_w^2 - \frac{\pi}{4} d_f^2}{\pi \cdot d_f} \quad (\text{S21})$$

where  $l_w$  (m) is the channel width and  $d_f$  (m) is the average channel dimension estimated by SEM.

The characteristic reaction time  $t_r$  (s) is determined by [73]:

$$t_r = \frac{C_{CH_4, in}}{r_{CH_4} \cdot \rho_c} \quad (S22)$$

where  $C_{CH_4, in}$  is the concentration of  $CH_4$  in the feed mixture ( $\text{kmol m}^{-3}$ ),  $r_{CH_4}$  is the observed reaction rate for  $CH_4$  ( $\text{kmol m}^{-3} \text{s}^{-1}$ ), and  $\rho_c$  is the density of the catalytic layer ( $\text{kg m}^{-3}$ ).

The longitudinal diffusion time  $t_z$  (s) is determined by [49]:

$$t_z = \frac{L_m^2}{D_{CH_4-mix}} \quad (S23)$$

where  $L_m$  is the monolith length (m) and  $D_{CH_4-mix}$  is the diffusivity of  $CH_4$  in gas phase ( $\text{m}^2 \text{s}^{-1}$ ).

#### A.4 External and internal mass transfer analysis

##### A.4.1 Characteristic dimensions for the external and internal mass transfer analysis

In order to study the external and internal mass transfer resistances, two different characteristic cross-sectional areas for a single channel of the monolith are defined: the cross-sectional area of gas phase or circular flow area  $A_{\Omega e}$  ( $\text{m}^2$ ) and the cross-sectional area of coated catalyst layer  $A_{\Omega i}$  ( $\text{m}^2$ ).

The cross-sectional area of fluid phase  $A_{\Omega e}$  ( $\text{m}^2$ ) is calculated as:

$$A_{\Omega e} = \frac{\pi \cdot d_f^2}{4} \quad (S24)$$

where  $d_f$  (m) is the average channel dimension estimated by SEM.

The cross-sectional area of coated catalyst layer  $A_{\Omega i}$  ( $\text{m}^2$ ) is calculated as:

$$A_{\Omega i} = A_{ch} - A_c \quad (S25)$$

where  $A_{ch}$  is the area of a single bare channel ( $\text{m}^2$ ) and  $A_c$  is the area remaining available in the channel for the flow of reactants after catalyst deposition ( $\text{m}^2$ ). For the channel shape under consideration (square channel with circular flow area),  $A_c$  ( $\text{m}^2$ ) corresponds with the circular flow area  $A_{\Omega e}$  ( $\text{m}^2$ ).

The area of a single bare channel  $A_{ch}$  ( $\text{m}^2$ ) is calculated as:

$$A_{ch} = l_w^2 \quad (S26)$$



where  $l_w$  (m) is the channel width.

Thus, it is possible to define the characteristic length scales for the fluid phase  $R_{\Omega e}$  (m) and for the coated catalyst layer  $R_{\Omega i}$  (m).

The characteristic length scale for the fluid phase  $R_{\Omega e}$  (m) is defined as [47]:

$$R_{\Omega e} = \frac{A_{\Omega e}}{P_c} \quad (\text{S27})$$

where  $A_{\Omega e}$  (m<sup>2</sup>) is the flow area (or cross-sectional area of fluid phase) and  $P_c$  (m) is the fluid-coated catalyst layer interfacial perimeter.

The fluid-coated catalyst layer interfacial perimeter is calculated as:

$$P_c = \pi \cdot d_f \quad (\text{S28})$$

Thus, the characteristic length scale for the fluid phase  $R_{\Omega e}$  (m) can be expressed as:

$$R_{\Omega e} = \frac{\frac{\pi d_f^2}{4}}{\pi d_f} = \frac{d_f}{4} \quad (\text{S29})$$

The characteristic length scale for the coated catalyst layer  $R_{\Omega i}$  (m) is defined as [47]:

$$R_{\Omega i} = \frac{A_{\Omega i}}{P_c} \quad (\text{S30})$$

where  $A_{\Omega i}$  (m<sup>2</sup>) is the cross-sectional area of coated catalyst layer and  $P_c$  (m) is the fluid-coated catalyst layer interfacial perimeter.

Thus, the characteristic length scale for the coated catalyst layer  $R_{\Omega i}$  (m) can be expressed as:

$$R_{\Omega i} = \frac{l_w^2 \frac{\pi d_f^2}{4}}{\pi d_f} \quad (\text{S31})$$

#### A.4.2 External and internal mass transfer coefficients

The external mass transfer coefficient  $k_{m,e}$  (m s<sup>-1</sup>) between the bulk of fluid phase and the fluid-coated catalyst layer interface is calculated as [47]:

$$k_{m,e} = \frac{Sh_e \cdot D_{CH_4-mix}}{4 \cdot R_{\Omega e}} \quad (\text{S32})$$

where  $Sh_e$  is the external Sherwood number,  $D_{CH_4-mix}$  is the diffusivity of CH<sub>4</sub> in gas phase (m<sup>2</sup> s<sup>-1</sup>) and  $R_{\Omega e}$  is the characteristic length scale for the fluid phase (m).

The internal mass transfer coefficient  $k_{m,i}$  (m s<sup>-1</sup>) between the interior of the coated catalyst layer and fluid-coated catalyst layer interface is calculated as [47]:

$$k_{m,i} = \frac{Sh_i \cdot D_{CH_4,e}}{R_{\Omega i}} \quad (S33)$$

where  $Sh_i$  is the internal Sherwood number,  $D_{CH_4,e}$  is the effective diffusivity of  $CH_4$  in the coated layer ( $m^2 s^{-1}$ ) and  $R_{\Omega i}$  is the characteristic length scale for the coated catalyst (m).

The external Sherwood number  $Sh_e$  is calculated by [47]:

$$Sh_e = Sh_{e\infty} + \frac{2.8}{Sc^{1/6}} \cdot \sqrt{P} \quad (S34)$$

where  $Sh_{e\infty}$  is the asymptotic external Sherwood number,  $Sc$  is the Schmidt ( $Sc$ ) number and  $P$  is the transverse Peclet number. For square channel,  $Sh_{e\infty} = 2.98$ . The transverse Peclet number is calculated as [47]:

$$P = \frac{R_{\Omega e}^2 \cdot u_o}{L_m \cdot D_{CH_4-mix}} \quad (S35)$$

where  $R_{\Omega e}$  is the characteristic length scale for the fluid phase (m),  $u_o$  is the inlet gas velocity at operative conditions ( $m s^{-1}$ ),  $L_m$  is the monolith length (m) and  $D_{CH_4-mix}$  is the diffusivity of  $CH_4$  in gas phase ( $m^2 s^{-1}$ ).

The internal Sherwood number  $Sh_i$  is calculated by [47]:

$$Sh_i = Sh_{i\infty} + \frac{\Lambda \cdot \varnothing^2}{1 + \Lambda \cdot \varnothing} \quad (S36)$$

where  $Sh_{i\infty}$  is the asymptotic internal Sherwood number,  $\Lambda$  is a constant that depends on the coated catalyst layer shape and kinetic parameters and  $\varnothing$  is the Thiele modulus.

The Thiele modulus  $\varnothing$  for a first order reaction is defined as:

$$\varnothing = \sqrt{\frac{k_{obs} \cdot R_{\Omega i}^2}{D_{CH_4,e}}} \quad (S37)$$

where  $k_{obs}$  is the observed first-order reaction rate constant ( $s^{-1}$ ),  $R_{\Omega i}$  is the effective transverse diffusion length in the coated catalyst layer (m) and  $D_{CH_4,e}$  is the effective diffusivity of  $CH_4$  ( $m^2 s^{-1}$ ).

The effectiveness factor  $\eta$  for a first order reaction can be expressed as [47]:

$$\eta = \frac{1}{1 + \frac{\varnothing^2}{Sh_i}} \quad (S38)$$

where  $\varnothing$  is the Thiele modulus for a first order reaction and  $Sh_i$  is the internal Sherwood number.

### A.4.3 Multiple resistances in series approach

The overall resistance for mass transfer  $R_t$  ( $s\ m^{-1}$ ) is defined as [47]:

$$R_t = R_e + R_i + R_r \quad (S39)$$

where  $R_e$  is the resistance for the external mass transfer ( $s\ m^{-1}$ ),  $R_i$  is the resistance for the internal mass transfer ( $s\ m^{-1}$ ) and  $R_r$  is the reaction resistance ( $s\ m^{-1}$ ). The resistance for the external mass transfer  $R_e$  ( $s\ m^{-1}$ ) can be calculated as:

$$R_e = \frac{1}{k_{m,e}} \quad (S40)$$

where  $k_{m,e}$  is the external mass transfer coefficient between the bulk of fluid phase and the fluid-coated catalyst layer interface ( $m\ s^{-1}$ ).

The resistance for the internal mass transfer  $R_i$  ( $s\ m^{-1}$ ) can be calculated as:

$$R_i = \frac{1}{k_{m,i}} \quad (S41)$$

where  $k_{m,i}$  is the internal mass transfer coefficient between the interior of the coated catalyst layer and fluid-coated catalyst layer interface ( $m\ s^{-1}$ ).

The reaction resistance  $R_r$  ( $s\ m^{-1}$ ) can be calculated as:

$$R_t = \frac{1}{k_{obs} \cdot R_{\Omega i}} \quad (S42)$$

where  $R_{\Omega i}$  (m) is the characteristic length scale for the coated catalyst layer and  $k_{obs}$  ( $s^{-1}$ ) is the observed first-order reaction rate constant.

Thus, the apparent (or overall experimentally observable) mass transfer coefficient  $k_{m,app}$  ( $m\ s^{-1}$ ) can be calculated as [47]:

$$\frac{1}{k_{m,app}} = \frac{1}{k_{m,e}} + \frac{1}{k_{m,i}} + \frac{1}{k_{obs} \cdot R_{\Omega i}} \quad (S43)$$

where  $k_{m,e}$  is the external mass transfer coefficient between the bulk of fluid phase and the fluid-coated catalyst layer interface ( $m\ s^{-1}$ ),  $k_{m,i}$  is the internal mass transfer coefficient between the interior of the coated catalyst layer and fluid-coated catalyst layer interface ( $m\ s^{-1}$ ),  $k_{obs}$  is the observed first-order reaction rate constant ( $s^{-1}$ ) and  $R_{\Omega i}$  is the characteristic length scale for the coated catalyst layer (m).

Writing S.43 in dimensionless form gives:

$$\frac{1}{k_{m,app}} \cdot \frac{D_{CH_4-mix}}{4 \cdot R_{\Omega e}} = \left( \frac{1}{Sh_e} + \frac{R_{\Omega i} \cdot D_{CH_4-mix}}{4 \cdot R_{\Omega e} \cdot D_{CH_4,e} \cdot Sh_i} + \frac{D_{CH_4-mix}}{4 \cdot R_{\Omega e} \cdot k_{obs} \cdot R_{\Omega i}} \right) \quad (S44)$$

$$\frac{1}{Sh_{app}} = \left( \frac{1}{Sh_e} + \frac{\alpha\beta}{4} \cdot \frac{1}{Sh_i} + \frac{\alpha\beta}{4\phi^2} \right) \quad (S45)$$

where the various dimensionless groups appearing in S.45 are defined as:

$$\beta = \frac{R_{\Omega i}}{R_{\Omega e}}, \quad \alpha = \frac{D_{CH_4-mix}}{D_{CH_4,e}}, \quad \phi^2 = \frac{k_{obs} \cdot R_{\Omega i}^2}{D_{CH_4,e}}, \quad Sh_{app} = \frac{4 \cdot k_{m,app} \cdot R_{\Omega e}}{D_{CH_4-mix}} \quad (S46)$$

where  $k_{m,app}$  ( $m \cdot s^{-1}$ ) is the apparent (or overall experimentally observable) mass transfer coefficient,  $D_{CH_4,e}$  is the effective diffusivity of  $CH_4$  ( $m^2 \cdot s^{-1}$ ),  $D_{CH_4-mix}$  is the diffusivity of  $CH_4$  in gas phase mixture ( $m^2 \cdot s^{-1}$ ),  $R_{\Omega i}$  is the characteristic length scale for the coated catalyst layer (m),  $R_{\Omega e}$  is the characteristic length scale for the fluid phase (m),  $Sh_i$  is the internal Sherwood number,  $Sh_e$  is the external Sherwood number,  $k_{obs}$  is the observed first-order reaction rate constant ( $s^{-1}$ ),  $\phi$  is the Thiele modulus for a first order reaction and  $Sh_{app}$  is the apparent (or experimentally observed) mass transfer coefficient.

In kinetic regime, the apparent mass transfer coefficient can be written as:

$$Sh_{app,kin} = \frac{4 \cdot \phi^2}{\alpha \beta} \quad (S47)$$

## A.5 Heat transfer effects

For highly endothermic reactions such as methane steam reforming, temperature gradients between the gas phase and catalyst surface cannot be neglected. Under steady-state conditions, the rate of mass transfer of methane reactant from the gas phase mixture to the solid surface must be equal to the rate of methane reactant conversion by surface reaction:

$$k_{m,e} \cdot A_{\Omega e} \cdot (C_b - C_s) = k_s \cdot A_{\Omega e} \cdot C_s^n \quad (S48)$$

where  $k_s$  is the surface reaction rate constant,  $C_b$  is the concentration in the bulk of the gas phase ( $mol \cdot m^{-3}$ ),  $C_s$  is the concentration in the surface of the catalyst layer ( $mol \cdot m^{-3}$ ).

Assuming that the outer surface of the catalyst particle is uniformly accessible to the reagents, that is, the thickness of the concentration and thermal boundary layers over the particle surface has constant values. Since each section of the outer surface behaves kinetically the same as all other parts, steady-state analysis of such a system is essentially one-dimensional [45, 59]. Thus, the heat generated by the surface reaction can be calculated by multiplying the mass transfer rate with the heat of reaction per mol of reactant. At steady state, we can obtain:

$$k_{m,e} \cdot A_{\Omega e} \cdot (C_b - C_s) \cdot (\Delta H_r) = h_e \cdot A_{\Omega e} \cdot (T_b - T_s) \quad (S49)$$

Solving the temperature difference, the final expression is given by:

$$\frac{k_{m,e}}{h_e} \cdot (C_b - C_s) \cdot (\Delta H_r) = (T_b - T_s) \quad (\text{S50})$$

where  $T_b, T_s$  is the temperature in the bulk of the gas phase and surface of the catalyst layer (K) respectively,  $\Delta H_r$  is the heat of MSR reaction ( $\text{J mol}^{-1}$ ) and  $h_e$  is the heat transfer coefficient associated for the gas phase ( $\text{W m}^{-2} \text{K}^{-1}$ ).

Hence, using the Chilton–Colburn analogy between heat and mass transfer ( $j_H \approx j_M$ ) for simple gas mixture, we can replace the ratio  $\frac{k_{m,e}}{h_e}$  and obtain the following expression [45, 59]:

$$k_{m,e} = \frac{j_M \cdot G}{\rho_f \cdot Sc^{\frac{2}{3}}} \quad h_e = \frac{j_H \cdot G \cdot Cp_f}{Pr^{\frac{2}{3}}} \quad (\text{S51})$$

$$(T_b - T_s) = \frac{\Delta H_r}{\rho_f \cdot Cp_f} \cdot \left(\frac{Pr}{Sc}\right)^{\frac{2}{3}} \cdot (C_b - C_s) \quad (\text{S52})$$

Considering the Lewis ( $Le$ ) and Carberry ( $Ca$ ) number, we can obtain the final expression as [45, 59]:

$$Le = \frac{Sc}{Pr} \quad Ca = \frac{C_b - C_s}{C_b} \quad (\text{S53})$$

$$(T_b - T_s) = \left(\frac{\Delta H_r \cdot C_b}{\rho_f \cdot Cp_f}\right) \cdot Le^{-2/3} \cdot Ca \quad (\text{S54})$$

where  $\rho_f$  is the density of the gas phase ( $\text{Kg m}^{-3}$ ),  $c_{p,f}$  is the heat capacity of the gas phase ( $\text{J Kg}^{-1} \text{K}^{-1}$ ) and  $Pr$  is the Prandtl number.

Thus, by dividing Eq. S.53 by  $T_b$ , it is possible to obtain the dimensionless external Prater number ( $\beta_{ext}$ ) which represents the ratio of the maximum heat consumption and heat transfer rates:

$$\frac{T_s}{T_b} = 1 - \left(\frac{\Delta H_r \cdot C_b}{\rho_f \cdot Cp_f}\right) \cdot \frac{1}{T_b} \cdot Le^{-2/3} \cdot Ca \quad (\text{S55})$$

$$\frac{T_s}{T_b} = 1 - \frac{\Delta T_{ad}}{T_b} \cdot Le^{-2/3} \cdot Ca \quad (\text{S56})$$

$$\frac{T_s}{T_b} = 1 - \beta_{ext} \cdot Ca \quad (\text{S57})$$

where  $\Delta T_{ad}$  is the adiabatic temperature rise ( $\Delta T_{ad} = \frac{\Delta H_r \cdot C_b}{\rho_f \cdot Cp_f}$ ; K) and  $\beta_{ext}$  is the dimensionless external Prater number ( $\beta_{ext} = \frac{\Delta T_{ad}}{T_b} \cdot Le^{-2/3}$ ).

The interphase heat transfer limitations can be evaluated using the criterion derived by Mears [61] (Eq. S.58) with the perturbation approach, in which the heat transfer resistance of the fluid phase is assumed to be lumped at the surface:

$$\chi = \frac{(\Delta H \cdot R^{obs} \cdot R_{\Omega e})}{h_e \cdot T_b} < \frac{0.15}{\gamma_b}; \quad \gamma_b = \frac{E_{act}}{R_g \cdot T_b} \quad (S58)$$

where  $R^{obs}$  is the observed reaction rate ( $\text{mol m}^3 \text{s}^{-1}$ ),  $h_e$  is the heat transfer coefficient associated for the gas phase ( $\text{W m}^{-2} \text{K}^{-1}$ ),  $R_g$  is the gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $E_{act}$  is the apparent activation energy of the reaction ( $\text{J mol}^{-1}$ ),  $\chi$  is the Damkohler for interphase heat transport and  $\gamma_b$  is the Arrhenius number evaluated at the bulk of the gas phase.

Anderson in 1963 [62] applied the perturbation approach to derive a criterion for the lack of importance of temperature gradients in catalyst particles. The reaction is assumed to follow Arrhenius temperature dependence and this criterion is valid regardless of whether there are diffusion limitations in the particle or not:

$$\frac{(\Delta H \cdot R^{obs} \cdot R_{\Omega i}^2)}{\lambda_{cat} \cdot T_s} < \frac{0.75}{\gamma_s} \quad (S59)$$

$$\psi = \frac{(\Delta H \cdot R^{obs} \cdot R_{\Omega i}^2)}{\lambda_{cat} \cdot T_s}; \quad \gamma_s = \frac{E_{act}}{R_g \cdot T_s} \quad (S60)$$

where  $\lambda_{cat}$  is the thermal conductivity of the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst ( $\text{W m}^{-1} \text{K}^{-1}$ ),  $\psi$  is the Damkohler for intraparticle heat transport and  $\gamma_s$  is the Arrhenius number evaluated at the surface of the gas phase.

In order to study the effects of mass and heat transfer, both balances must be solved simultaneously to estimate the concentration and temperature profile. From the mass balance, we can write the following expression:

$$D_e \cdot \frac{d^2 c}{dx^2} - (-R) = 0 \quad (S61)$$

The heat balance can be written as:

$$\lambda_e \frac{d^2 T}{dx^2} - (-R) \cdot (\Delta H_r) = 0 \quad (S62)$$

where  $\lambda_e$  is the effective thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ ). Considering that the reaction rate ( $R$ ) is the same in both balances, we can obtain the following expression:

$$\frac{D_e \cdot (\Delta H_r)}{\lambda_e} \cdot \frac{d^2 c}{dx^2} = \frac{d^2 T}{dx^2} \quad (S63)$$

By integrating the Equation S.63 and considering the surface concentration and temperature ( $C_s, T_s$ ), we can obtain the following linear expression between internal temperature and reactant concentration [15,16]:

$$(T_s - T_{b,c}) = (\Delta H_r) \cdot \frac{D_e}{\lambda_e} \cdot (C_s - C_{b,c}) \quad (\text{S64})$$

where  $T_{b,c}$  is the temperature in the bulk of the catalyst layer (K) and  $C_{b,c}$  is the concentration within the catalyst layer ( $\text{mol m}^{-3}$ ). It is worth noting the largest possible temperature difference into the catalyst layer is attained when the concentrations within the bulk of the catalyst layer becomes zero, hence we can refer the maximum temperature difference ( $\Delta T_{max}$ ) to the surface temperature using the dimensionless internal Prater number ( $\beta_{in}$ ) by [15,16]:

$$\beta_{in} = \frac{\Delta T_{max}}{T_s} = \frac{(\Delta H_r) \cdot C_s}{T_s} \cdot \frac{D_e}{\lambda_e} \quad (\text{S65})$$

$\Sigma$	[cpsi]	100
$D_m$	[m]	0.030
$L_m$	[m]	0.0019
$\delta_w$	[m]	0.00063
$N$	[m]	0.1563
$E$	[-]	0.564
GSA	$[\text{m}^2 \text{m}^{-3}]$	1187,333
$d_h$	[m]	0.0019
$A_m$	[m]	0.00126

**Table A5.** Properties of the bare monolith.

T [°C]	$t_c$ [s]	$t_d^i$ [s]	$t_d^e$ [s]	$t_r$ [s]	$t_z$ [s]
550	0.3091	0.0456	0.0012	0.2238	5.1500
600	0.2914	0.0441	0.0010	0.1928	4.5926
650	0.2756	0.0428	0.0009	0.1883	4.1264
700	0.2615	0.0405	0.0008	0.1441	3.6903
750	0.2487	0.0394	0.0007	0.1151	3.3138
800	0.2371	0.0384	0.0007	0.0943	2.9217
850	0.2266	0.0384	0.0006	0.0939	2.6402

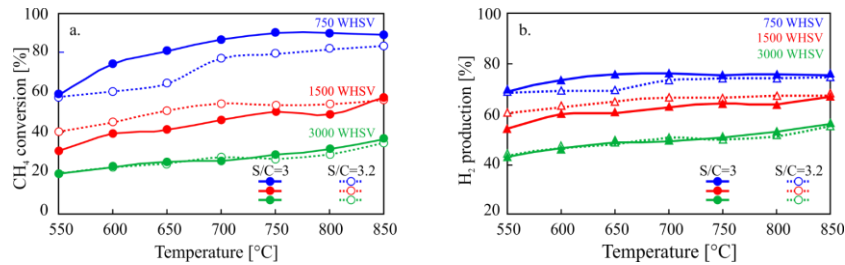
**Table A6.** Characteristic times for the 1.5Ru5Al catalyst.

T [°C]	$t_c$ [s]	$t_d^i$ [s]	$t_d^e$ [s]	$t_r$ [s]	$t_z$ [s]
550	0.3091	0.0714	0.0010	0.1521	4.5226
600	0.2914	0.0691	0.0008	0.1212	3.9330
650	0.2756	0.0670	0.0007	0.1113	3.4816
700	0.2614	0.0651	0.0007	0.1040	3.1674
750	0.2487	0.0634	0.0006	0.1001	2.9079
800	0.2371	0.0618	0.0006	0.1001	2.6688
850	0.2266	0.0604	0.0005	0.1014	2.4751

**Table A7.** Characteristic times for the 1.5Ru10Al catalyst.

T [°C]	$t_c$ [s]	$t_d^i$ [s]	$t_d^e$ [s]	$t_r$ [s]	$t_z$ [s]
550	0.3091	0.1319	0.0008	0.4222	4.7509
600	0.2914	0.1277	0.0008	0.3860	4.2279
650	0.2756	0.1239	0.0007	0.3713	3.8065
700	0.2614	0.1204	0.0006	0.3459	3.4299
750	0.2487	0.1172	0.0006	0.3495	3.1437
800	0.2371	0.1142	0.0005	0.3401	2.8716
850	0.2266	0.1115	0.0005	0.3195	2.6049

**Table A8.** Characteristic times for the 1.5Ru20Al catalyst.



**Fig. A1.** MSR tests, performance comparison of monoliths 1.5% Ru on 10%  $\gamma$ - $\text{Al}_2\text{O}_3$  at various WHSV and S/C a)  $\text{CH}_4$  conversion; b)  $\text{H}_2$  production.

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