

CATALYTIC SYNTHESIS GAS PRODUCTION IN
MICROCHANNEL REACTORS

by

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ABSTRACT

CATALYTIC SYNTHESIS GAS PRODUCTION IN MICROCHANNEL REACTORS

This dissertation presents syngas production from methane by steam and oxidative steam reforming in novel design wall-coated and packed microchannel reactors over δ - Al_2O_3 supported Ni and precious metal (Rh, Ru, Pd, Pt) based catalysts. Firstly, experimental design for determining performance test conditions was conducted to investigate the effects of reaction temperature, molar steam-to-carbon (S/C) ratio, particle size and addition of carbon dioxide to the feed over various catalysts including Ni/ δ - Al_2O_3 , Pt-Ni/ δ - Al_2O_3 , Pd/ δ - Al_2O_3 , Rh/ δ - Al_2O_3 and Ru/ δ - Al_2O_3 for MSR activity. The aim of second part of the study was to investigate and compare methane steam reforming (MSR) performances of precious metal and nickel catalysts, 2wt% Rh, 2wt% Ru, 2wt% Pd, and 10wt% Ni, for syngas production in two different microchannel reactor geometries, namely wall-coated and packed microchannels, operated at 873-1023 K and S/C ratios of 2.5-3.5, using a fixed inlet methane concentration and identical contact time of $7.22 \text{ mg}\cdot\text{min}\cdot\text{cm}^{-3}$. In both cases, H_2 and CO production rates over 2wt% Rh were the highest. It was found that H_2/CO molar ratios in coated microchannel product streams are significantly lower than those in packed microchannels, 2wt% Rh is better in terms of CO selectivity while 10wt% Ni gives the highest H_2 selectivity. Thirdly, oxidative steam reforming of methane (OSRM) performance of 0.2wt%Pt-2wt%Rh/ δ - Al_2O_3 bimetallic catalyst was investigated in packed microchannel reactors, and compare its performance with coated microchannels, a parametric study- involving variations in reaction temperature, contact time, and steam-to-carbon and oxygen-to-carbon ratios was performed in the relatively lower contact time range of 0.41 to $0.71 \text{ mg}\cdot\text{min}\cdot\text{cm}^{-3}$. Increase in all of the parameter values led to improvement in methane conversion, while CO selectivity increased only with temperature and contact time. In all cases, methane conversions in both microchannel configurations are found to be comparable with each other. CO selectivity, a critical parameter in syngas production, is found to be significantly higher in the coated microchannel configuration.

ÖZET

MİKROKANAL REAKTÖRLERDE KATALİTİK SENTEZ GAZI ÜRETİMİ

Bu doktora tezi, özgün tasarımı duvara kaplamalı ve tanecik dolgulu mikrokanal reaktörlerde, δ - Al_2O_3 destekli Ni ve kıymetli metal (Rh, Ru, Pd, Pt) bazlı katalizörler üzerinde metandan sentez gazı üretimini ele almaktadır. Öncelikle, tepkime sıcaklığının, molar buhar/karbon oranının, tanecik boyutunun ve beslemedeki karbondioksit varlığının ve tümü δ - Al_2O_3 destekli Ni, Pt-Ni, Pd, Rh, Ru gibi katalizörlerin, metanın buhar reformlanması (MSR) verimine olan etkilerini araştırmak üzere test koşulları belirlenmiştir. Çalışmanın ikinci kısmında, duvara kaplamalı ve tanecik dolgulu mikrokanal olmak üzere iki farklı reaktör tasarımında %2 Rh, %2 Ru, %2 Pd ve %10 Ni katalizörlerin metan buhar reformlanması aktiviteleri, tepkime sıcaklığı 873-1023 K, buhar/karbon oranı 2.5-3.5 aralıklarında değiştirilerek, ve kalma süresi $7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ değerinde tutularak, sabit bir metan giriş oranında araştırılmış ve iki reaktör tasarımı karşılaştırılmıştır. Her iki reaktör düzeninde %2 Rh, en yüksek H_2 ve CO üretim hızlarını vermiştir. Duvara kaplamalı reaktörde elde edilen H_2/CO oranlarının tanecik dolgulu reaktördekilerden daha düşük olduğu belirlenmiştir. CO seçiciliği bakımından %2 Rh daha iyi sonuç verirken, %10 Ni en yüksek H_2 seçiciliğini göstermiştir. Üçüncü olarak, δ - Al_2O_3 destekli, çift metalli %0.2 Pt-%2 Rh katalizörünün metanın oksijenli buhar reformlanması (OSRM) sürecindeki verimi tanecik dolgulu mikrokanal reaktörde incelenmiş ve bu sonuçlar duvar kaplamalı mikrokanal reaktör sonuçları ile karşılaştırılmıştır. Burada incelenen temas süresi aralığı olan 0.41 - $0.71 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$, diğer deneylere göre daha düşüktür. Çalışılan bütün parametrelerdeki (tepkime sıcaklığı, temas süresi, buhar/karbon oranı ve oksijen/karbon) artış metan dönüşümünü artırırken, sadece tepkime sıcaklığı ve temas süresindeki artış CO seçiciliği arttırmaktadır. Bütün parametreler için, metan dönüşüm değerleri her iki reaktör düzeni için karşılaştırılabilir düzeydedir. Sentez gazı üretiminde önem arzeden CO seçiciliğinin duvar kaplamalı mikrokanal reaktör düzeninde belirgin bir şekilde daha yüksek çıktığı bulunmuştur.

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LIST OF SYMBOLS

r_A	Reaction rate of A
X_A	Conversion of A
S_A	Selectivity of A

LIST OF ACRONYMS/ABBREVIATIONS

CI	Co-impregnation
CP	Co-precipitation
CVD	Chemical vapor deposition
DP	Deposition precipitation
HM	Hydrothermal method
HP	Homogenous precipitation
IMM	Mainz institute of microtechnology
IWI	Incipient to wetness impregnation
MSR	Methane steam reforming
OSRM	Oxidative steam reforming of methane
PEMFC	Polymer electrolyte membrane fuel cell
PVD	Physical vapor deposition
POX	Partial oxidation
RTD	Residence time distribution
SI	Sequential impregnation
SP	Sequential precipitation
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TOX	Total oxidation
TPR	Temperature programmed reaction
VLSI	Very large scale integrated
WGS	Water gas shift reaction
WI	Wet impregnation
XRD	X-ray diffraction

1. INTRODUCTION

Hydrogen is one of the oldest known molecules and is used extensively by many industries for a variety of applications. Most of its use is based on its reactivity rather than its physical properties. Recently its use in petroleum refining has been growing very rapidly due to a combination of factors relating to changes in the quality of crude oil; environmental regulations such as limits of sulfur in diesel, allowable limits of NO, and SO in off-gas emissions to the atmosphere, as well as the aromatic and light hydrocarbon concentrations in gasoline (Ramachandran and Menon, 1998).

In greater part of applications where hydrogen is used as a reactant, hydrogenation takes place to insert hydrogen to saturate or to cleave molecules for removing hetero atoms such as sulfur and nitrogen. In most of these processes, reaction depends on hydrogen partial pressure, and hence, high purities and high pressures are employed in the process. Majority of hydrogen is used as a reactant in the chemical and petroleum industries. Among the most important uses, ammonia production accounts for almost 50%; petroleum processing about 37%; methanol production 8% (Czuppon *et al.*, 1995). The usage in petroleum processing is expected to increase rapidly due to various environmental regulations.

Automotive exhaust is currently a major pollution source. Fuel cells with their high energy conversion efficiency (50–70%) and zero or nearly zero emission are the best candidates for pollution-free and energy-saving power supply for mobile and stationary applications. Among the several different types of fuel cells, the polymer electrolyte (or proton-exchange) membrane fuel cell (PEMFC) fuelled by H₂ is the most promising option for transportation applications because of its lower operating temperature, higher power density, higher energy efficiency, and fast response (Ralph, 1999; Peijun *et al.*, 2004). Hydrogen is the fuel for PEMFCs. On-board generation of hydrogen from hydrocarbons is known as one of the most practical ways for PEMFC-driven vehicles (Borup *et al.*, 2005). However, miniaturization of the hydrogen source is a prerequisite for its commercial application (Choi and Stenger, 2002; Tonkovich *et al.*, 1999).

In steam-reforming (SR), water vapor reacts with the primary hydrocarbon fuel, forming carbon monoxide, carbon dioxide, and hydrogen. The equilibrium amounts of these products depend strongly on temperature, less strongly on pressure. The higher the temperature, the greater is the amount of CO in the product (Peijun *et al.*, 2004). Steam-reforming is always endothermic, so external energy must be supplied for this reaction.

In partial oxidation (POX), the primary hydrocarbon fuel reacts with oxygen in an inadequate quantity for CO-producing combustion. Partial oxidation is exothermic, so does not need a supply of energy. Nevertheless, the overall efficiency can suffer because of waste heat production. To prevent excessive temperature increase, steam is usually added to the feed (Brejc *et al.*, 1989), which reacts endothermically with the primary fuel. POX has some aspects of auto-thermal reforming (ATR), which combines steam-reforming and oxidation, and in ATR oxidation of the hydrocarbon fuel supplies the energy required by the steam-reforming reaction.

Steam-reforming has wide industrial applications. Ammonia and methanol synthesis employ steam-reforming of natural gas as their first step. The steam-reforming of other hydrocarbons is also widely used for generating hydrogen and synthesis gas. Steam reforming of natural gas or methane is a nickel-catalyzed process occurring at 1000–1100 K, while steam-reforming of other hydrocarbons occurs at temperatures in the 1000–1150 K range (Czuppon *et al.*, 1995; Trimm and Önsan, 2001; Önsan, 2007). Therefore, heat management for SR has a crucial effect on the process performance. At this point, micro-structured reactors receive great attention because they present the possibility of solving heat transfer and large volume requirements as well as other issues involved in conventional reactors.

Micro-reaction technology is expected to provide a number of advantages in chemical production processes (Jensen, 2001). The high heat and mass transfer rates possible in microfluidic systems allow reactions to be conducted under more aggressive conditions with higher yields than can be achieved with conventional reactors. More importantly, new reaction pathways considered too difficult in conventional equipment, can be pursued using micro-channel reactors. Even if a microreactor fails, the small quantity of chemicals released accidentally can be easily contained. Moreover, the

presence of integrated sensor and control units allow the failed reactor to be isolated and replaced while other parallel units that can continue production. These inherent safety characteristics suggest that production scale systems of multiple microreactors should enable distributed point-of-use synthesis of chemicals with storage and shipping limitations, such as highly reactive and toxic intermediates (e.g., cyanides, peroxides, azides). As a demonstration of these concepts, DuPont has synthesized a number of potentially hazardous chemicals, including isocyanates, in a microreactor formed by bonding silicon wafers patterned to form channels, preheaters, and catalytic reactor sections (Lowe and Ehrfeld, 1999).

Microreactor concepts for heterogeneous gas phase reactions are not very common in reaction engineering on an industrial scale. These concepts often provide important compounds used for a large variety of different processes and products. Thermal conditions often have a huge impact on reaction conditions at catalyst surfaces. Microreactors already have proven their applicability for isothermal performance even for highly exothermic reactions (Ehrfeld *et al.*, 2000; Schwalbe *et al.*, 2004). Furthermore, micro-structured reactors are very useful tools for highly efficient heat transfer and dissipation. Based on these results, several investigations on the influence of heat management on liquid- and gas-phase reactions have been started. Meanwhile, these investigations include experiments on the influence of the thermal conditions at catalyst surfaces involved in gas phase reactions.

Great achievements have been reported in the new area of microreactor technology (Jahnisch *et al.*, 2004); Kolb and Hessel, 2004); it is now possible to use micro-channel reactors in the field of on-board PEMFC hydrogen source via hydrocarbon conversion (Holladay *et al.*, 2004). The small dimension of micro-channel geometry is favoring isothermal operating conditions due to high surface-to-volume ratio, enhanced heat and mass transfer and intrinsic safety. The application of micro-reaction technology can greatly improve the efficiency of systems and diminish their volumes and weights. Holladay *et al.* (2004) have presented a detailed discussion on the developments in portable hydrogen production using microreactor technology.

This dissertation presents syngas production from methane in novel design wall-coated and packed microchannel reactors over $\delta\text{-Al}_2\text{O}_3$ supported Ni and precious metal - Rh, Ru, Pd, Pt- based catalysts. Section 2 includes a literature survey about dimensional analysis of macro and micro-systems, advantages and micro-fabrication techniques of microreactors. In addition, hydrogen production from hydrocarbons via steam reforming, partial oxidation and auto-thermal reforming gas phase reactions in novel design microreactors is also presented. The experimental systems designed and used in this study as well as the details of all experimental work conducted are given in Section 3.

The Results and their Discussion are presented in three main sections. In the first part, Section 4.1, preliminary experiments conducted on steam methane reforming (SMR) in the conventional packed bed quartz micro-reactors over $\delta\text{-Al}_2\text{O}_3$ supported 0.2%Pt-10%Ni, 2%PM (PM= Rh, Ru, Pd) catalysts are presented and discussed. Experiments in this part of the study were performed in temperature range of 873 to 1023 K and atmospheric pressure with a steam-to-carbon ratio (S/C) range of 2.0 to 3.5 at various feed flowrates and weight-based contact times.

In the second part, Section 4.2, MSR performances of precious metal and nickel catalysts, 2wt% Rh, 2wt% Ru, 2wt% Pd, and 10wt% Ni, for syngas production in two different microchannel reactor geometries, namely wall-coated and packed microchannels, operated at 873-1023 K and S/C ratios of 2.5-3.5, using a fixed inlet methane concentration and identical contact time of $7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ are compared and discussed.

In the third part of Results and Discussion, Section 4.3, Oxidative Steam Reforming of Methane (OSRM) to synthesis gas over the $\delta\text{-Al}_2\text{O}_3$ supported bimetallic 0.2%Pt-2%Rh catalyst was investigated in packed microchannel reactors. Methane conversion and CO selectivity in the product were investigated in terms of reaction temperature, molar steam-to-carbon (S/C) and oxygen-to-carbon (O_2/C) ratios, and contact time packed catalyst geometry. The results of OSRM were compared and discussed with coated-microchannel configuration experiments by Karakaya (2012). In addition to the bimetallic 0.2%Pt-2%Rh catalyst, the activity of monometallic 2%Rh catalyst for OSRM was also investigated in the packed microchannel configuration and compared with that of the bimetallic 0.2%Pt-2%Rh catalyst.

2. LITERATURE SURVEY

Microsized devices with characteristic flow passages that are less than 1 mm wide, but not so small that molecular effects would have to be accounted for, are analyzed systematically with respect to the appropriate way of modeling momentum and heat transfer. Based on the dimensional analysis of the underlying continuum equations (Navier–Stokes and first law of thermodynamics) scaling effects can be identified that characterize flow and heat transfer in small, microsized devices compared to the same geometries but on a macrosized scale (Figure 2.1).

As far as heat transfer is concerned variable property effects on the microscale turn out to be more important than in conventional macrosized devices. If, however, nondimensional quantities are introduced by referring all lengths to diameter and all other quantities like velocities and temperature to w_c and T , respectively, the question arises: what is “macro”, what is “micro”? Typical numbers are given for the parameters of a simple channel flow with heat transfer for a macro and a micro situation in Table 2.1. When the characteristic length scale D_h of a certain problem is decreased below 1 mm one by definition leaves the “macro-world” and enters the “micro-world” of momentum and heat transfer (Brand *et al.*, 2006).

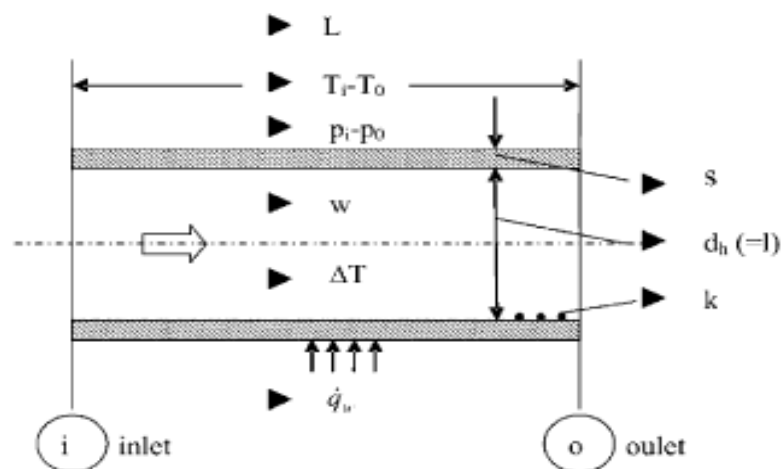


Figure 2.1. Schematic representation of micro and macro scale parameters.

Table 2.1. Dimensional numbers for micro and macro scale.

Parameter	Macro	Micro	Micro/macro
Pipe length L	10^{-1}m	10^{-2} m	0.1
Hydraulic diameter Dh (= l)	10^{-2}m	10^{-4} m	0.01
Wall thickness s	10^{-2}m	10^{-2}m	1
Wall roughness height k	10^{-4}m	10^{-6} m	0.01
Mean velocity w_c	1 m/s	1 m/s	1
Heat flux density q_w	10 W/m^2	10 W/m^2	1
Pressure drop $p_i - p_0$ $\Delta p = \frac{64}{\text{Re}} \frac{L}{l} \frac{\rho}{2} w^2$	10^{-2} mbar	10 mbar	1000
Temperature difference ΔT (wall–bulk) $\text{Nu} = \frac{\dot{q}_w l}{\lambda \Delta T} = \text{const.}$	$1\text{ }^{\circ}\text{C}$	$10^{-2}\text{ }^{\circ}\text{C}$	0.01
Temperature increase $T_0 - T_i$	$1\text{ }^{\circ}\text{C}$	$10\text{ }^{\circ}\text{C}$	10
$\Delta T / (T_0 - T_i)$ $\dot{m} c_p (T_0 - T_i) = \dot{q}_w \pi d_h L$	1	10^{-3}	0.001

2.1. Microstructured Reactors

A large number of applications within the last decade clearly demonstrated fundamental advantages for miniaturized analysis systems compared to lab-scale equipment. The smaller devices needed less space, materials and energy, and often had shorter response times. In particular, more information per space and time was gained. By parallel micro-fabrication and automated assembly, the costs per device could be kept low. Decreasing the component size, in addition, allowed the integration of a multitude of small functional elements, thereby enhancing the system performance.

Micro-structured reactors can be a valuable tool in the hands of an experienced chemist or reaction engineer. These reactors typically have heat exchange coefficients of at least 1 megawatt per cubic meter per Kelvin, up to $500 \text{ MW m}^{-3} \text{ K}^{-1}$ versus a few kilowatts in conventional glassware (1L flask $\sim 10 \text{ kW m}^{-3} \text{ K}^{-1}$). Therefore, micro-structured reactors can remove heat much more efficiently than vessels and even critical reactions such as nitration can be performed safely at high temperatures (Roberge *et al.*, 2005). Hot spot temperatures as well as the duration of high temperature exposition due to exothermicity decreases remarkably. Thus, micro-structured reactors may allow better kinetic investigations, because local temperature gradients affecting reaction rates are much smaller than in any batch vessel. Heating and cooling a micro-structured reactor is also much quicker and operating temperatures can be as low as 173 K. As a result of the superior heat transfer, reaction temperatures may be much higher than in conventional batch-reactors. Many low temperature reactions as organometallic chemistry can be performed in micro-structured reactors at temperatures of 263 K rather than at 223 K to 195 K as in laboratory glassware equipment.

Micro-structured reactors are generally operated continuously, which allows the subsequent processing of unstable intermediates and avoids typical batch workup delays. Especially low temperature chemistry with reaction times in the millisecond to second range are no longer stored for hours until dosing of reagents is finished and the next reaction step may be performed. This rapid work up avoids decay of precious intermediates

and often allows better selectivity (Schwalbe *et al.*, 2002). Continuous operation and mixing causes a very different concentration profile when compared with a batch process. In a batch, reagent A is filled in and reagent B is slowly added. Thus, B encounters initially a high excess of A. In a micro-structured reactor, A and B are mixed nearly instantly and B will be not exposed to a large excess of A. This may be an advantage or disadvantage depending on the reaction mechanism – it is important to be aware of such different concentration profiles.

Although a bench-top micro-channel reactor can synthesize chemicals only in small quantities, scale-up to industrial volumes is simply a process of multiplying the number of micro-channels. In contrast, batch processes too often perform well on R&D bench-top level but fail at batch pilot plant level (Schwalbe *et al.*, 2004).

Pressurization of materials within micro-channel reactors (and associated components) is generally easier than with traditional batch reactors. This allows reactions to be increased in reaction rate by raising the temperature beyond the boiling point of the solvent; the typical Arrhenius behavior is facilitated in micro-structured reactors and should be considered a key advantage. Pressurization may also allow dissolution of reactant gasses within the flow stream.

2.2. Physical Size Considerations

The volumes of micro-reactors are still too large in order to interact with reactants significantly on a molecular level. Their main impact focuses on intensifying mass and heat transport as well as improving flow patterns. Therefore, benefits concerning chemical engineering aspects are the main driver for micro-reactor investigations, while chemistry, in terms of reaction mechanism and kinetics, remains unchanged. It is possible to present the advantages of the micro-structured reactors in terms of advantages arising from the decrease in the size and the increase in the number of units.

2.2.1. Decrease in Linear Dimensions

For a given difference in a physical property, decreasing the linear dimensions increases the respective gradient. This refers to properties particularly important for processing in chemical reactors, such as temperature, concentration, density, or pressure. Consequently, the driving forces for heat transfer, mass transport or diffusion flux per unit volume or unit area increase when using micro-structured reactors. These simple theoretical predictions were evidenced by a number of studies concerning heat and mass transport.

The majority of today's micro-structured reactor/heat exchanger devices contain micro-channels with typical widths of 50 μm to 500 μm , with the separating wall material between reaction and heat transfer channels being kept down to 20 to 50 μm . As a result, heat transfer coefficients up to 25000 $\text{W}/\text{m}^2\text{K}$ measured in micro-devices exceed those of conventional heat exchangers by at least one order of magnitude (Schubert *et al.*, 1998). Typical fluid layer thicknesses in micro-mixers can be set to a few tens of micrometers in special configurations down to the nanometer range. Therefore, mixing times in micro-mixers come to milliseconds, even to nanoseconds in some cases (Branebjerg *et al.*, 1996; Knight *et al.*, 1998), which is hardly achievable using stirring equipment or other conventional mixers.

2.2.2. Increase in Surface-to-Volume Ratio

As a consequence of the decrease in fluid layer thickness, the corresponding surface-to volume ratio of the fluid entity is markedly increased. Specific surfaces of micro-channels are from 10000 to 50000 (m^2/m^3), whereas typical laboratory and production vessels usually do not exceed 1000 (m^2/m^3) and 100 (m^2/m^3), respectively. Apart from benefits of heat transfer, this increase in specific vessel surface can be utilized, e.g., in catalytic gas phase reactors coated with the active material on the inner walls. Similar benefits have to be expected for multiphase processes, when at least one of the fluid phases has a layer thickness in the micrometer range. Both estimations by theory and experiments proved that the specific interfaces of such multiphases in micro-structured reactors can be set in the range of 5000 to 30000 (m^2/m^3). So far, the highest reported interface was

measured using a falling film micro-structured reactor totaling $25000 \text{ (m}^2/\text{m}^3)$ (Ehrfeld *et al.*, 2000). Traditional bubble columns do not exceed a few $100 \text{ m}^2/\text{m}^3$; the best modern gas/liquid laboratory contactors such as impinging jets generate liquid surfaces of about $2000 \text{ (m}^2/\text{m}^3)$ (Herskowits *et al.*, 1990). In some favorable cases, e.g. regarding annular flow in micro bubble columns (Chambers and Spink, 1999), the corresponding specific interfaces can be set nearly as high as the specific surfaces of micro-channels, thus potentially achieving $50000 \text{ (m}^2/\text{m}^3)$ or even larger values. First measurements indeed showed large specific interfaces for this flow pattern, although not yet reaching the theoretically possible limit.

2.2.3. Decrease in Volume

As a result of the reduction in linear dimensions, the volume of micro-structured reactors is significantly decreased compared to large-scale reactors, typically amounting to a few μL . This difference becomes even larger when, in combination with reactor miniaturization, a large-scale batch process is replaced by continuous flow operation in micro-devices. In case of a metalloorganic reaction, the material hold-up could be decreased from a 6000 L tank to a volume of a few cm^3 within five miniaturized mixers. The smaller hold-up increases process safety and the shorter residence time improves selectivity.

2.2.4. Production Flexibility

An increase in throughput in micro-structured reactors is achieved by a numbering-up approach, rather than by scaling-up (Ehrfeld *et al.*, 2000). The functional unit of a micro-structured reactor, e.g. a mixing structure, is multiply repeated. Fluid connection between these units can be achieved by using distribution lines and flow equipartition zones, most likely hierarchically assembled. Numbering-up widely guarantees that desired features of a basic unit are kept when increasing the total system size. In an ideal case, measuring devices for process development and production reactor become similar, being composed of identical units. This was demonstrated by comparing the mixing quality of an array of ten mixing units with the performance of a single unit (Ehrfeld *et al.*, 2000). These results also showed the crucial importance of flow distribution for the efficiency of the

total reaction unit. A larger number of units also results in higher flexibility in adapting production rate to varying demand since, at least in principle, a certain number of systems can be switched off or further systems may be simply added to the production plant. A plant design based on a large number of small reaction systems can, again at least in principle, be modified to perform a variety of reactions by changing the piping network, i.e. the plant may be adapted to the synthesis of various substances using micro-structured reactor modules like a “LEGO” system. This flexibility may be supported by a much broader range of operating conditions of a micro-structured reactor compared with a macroscopic system.

In summary, micro-structured reactors are suitable for fast, highly exothermic or endothermic chemical reactions because they lead to:

- process intensification,
- inherent reactor safety,
- broader reaction conditions including up-to the explosion regime,
- distributed production,
- faster process development.

2.3. Fast and Cost-Saving Screening of Materials and Processes

Another application of micro-channel reactors is in combinatorial studies. Recently, the application of combinatorial strategies has been more and more extended from drug development in pharmacy to screening of inorganic materials, catalysts and polymers. Whilst the former processing route was focused on the use of small batch reaction vessels, so-called micro/nano titer plates, the latter approaches demand a diversification of reactor types. So far, inorganic materials, and in selected cases catalysts, were tested as arrays of spatially separated thin zones consisting of different materials. These zones were usually coated on wafers by means of thin film deposition techniques, in most cases using mask processes in order to locally change material properties, e.g. generating concentration

profiles. However, this straightforward approach is limited, especially regarding catalyst and polymer material research. The need for support porosity in the former case and long reaction times in the latter case are two among several arguments favoring the use of tubular continuous flow reactors. A combined processing in many small tubes in parallel was already realized in flow-through tube reactors (Ehrfeld *et al.*, 2000). A further decrease in hydraulic diameter leads to more and more compact micro-structured reactor design.

First design concepts for such screening micro-structured reactors were a stack providing a frame for insertion of disposable catalyst carrier plates and a sheet consisting of a number of reaction plates, structurally analogous to a titer plate. Apart from increasing the number of samples to be investigated, further benefits in screening micro-structured reactors are the rapid and precise change of temperature, concentration and pressure. In particular, the possibility of isothermal operation and the high efficiency of mass transfer provide a sound information base, e.g. allowing the measurement of intrinsic kinetic properties. Although screening in micro-structured reactors is most often performed by parallel processing, the continuous flow operation of micro-structured reactors enables rapid serial synthesis as well. Due to interdependence of sample generation and testing, screening is, among all application fields of micro-structured reactors, strongly dependent on the development of a practical total system approach, combining all relevant components in one device (Ehrfeld *et al.*, 2000).

2.4. Fabrication of Microstructured Reactors

The following technologies have been preferably applied for fabrication of micro-structured reactors at present:

- Bulk micromachining of monocrystalline materials, e.g. silicon, using anisotropic wet chemical etching (Angell *et al.*, 1993)
- Dry etching processes using low pressure plasma or ion beams (reactive ion etching, reactive ion beam etching)

- A combination of deep lithography, electroforming and molding, micromachining with laser radiation (LIGA process)
- Micromolding, e.g. using mold inserts machined by precision engineering techniques
- Wet chemical etching of glass including anisotropic etching of photosensitive glass
- Advanced mechanical milling, turning, sawing, embossing, punching, and drilling processes based on precision engineering
- Isotropic wet chemical etching, e.g. of metal foils with a resist pattern
- Micro electro discharge machining (EDM)
- Laser ablation.

Several technologies are usually combined in a process line for fabricating micro-structured reactors so that these technologies can be regarded like tool machines in a micro workshop. In addition, auxiliary processes ranging from thin film technologies to mechanical surface modification belong to the tool assembly of this micro workshop as well as test equipment and design and simulation software.

The availability of the necessary fabrication equipment is perhaps the key factor in the choice of substrate material for chip manufacturing. This may explain the extensive use of photolithography and wet etching of glass or silicon substrates. Other important factors in the choice of material include the chemical compatibility and internal surface characteristics. With the increasing number of etching and deposition methods available, the diversity of substrate material has increased, now including polymers and plastics (McCreedy, 2000).

For the purpose of syngas production in constructs stainless steel micro-structured reactors at relatively high temperatures (higher than 650 °C), two techniques used for

metallic material shaping will be introduced here in greater detail: (a) photolithography and wet etching, (b) EDM for micro fabrication and (c) lamination.

2.4.1. Photolithography and wet etching

In this method, the substrate is first coated with a layer of vapor-deposited metal, e.g. chromium, a few hundred Å thick on top of which a photo-resist layer is spin-coated. The required channel configuration is prepared in mask form. By exposing the photo-resist to an UV light source with the mask covering the chip, it is possible to transfer the desired pattern to the chip. The exposed photo-resist (the channels) can then be removed and the now bare metal layer etched away. The desired channel pattern is then marked out on the surface of the chip in terms of exposed substrate surface, while the rest of the chip remains protected. An appropriate etching solution is used to cut the channel into the glass, a process that can take from few minutes to several hours. A number of factors influence the rate of etching, including the hardness of the glass (where glass is the substrate), the concentration of the etchant, temperature, extent of the agitation and the required channel depth (McCreedy, 2000).

Although method of wet chemical etching can be convenient for some materials such as silicon with high aspect ratios and precision engineering features, for some materials such as glass, it is possible to obtain non-parallel walls because the etching process occurs on the exposed glass surface, and hence, as the channel etches deeper, the walls are also etched, thus, channels wider at the top than at the base (Fister *et al.*, 1998). This phenomenon is an obvious limitation, which will prevent the etching of deep narrow channels.

2.4.2. EDM for Micro Fabrication

A machining method typically used for hard metals, Electrical Discharge Machining makes it possible to work with metals for which traditional machining techniques are ineffective. Sparks between electrically conductive workpiece and electrode separated by a dielectric liquid like DI (deionized) water or oil are formed. Every spark melts and

evaporates a tiny amount of the workpiece which is flushed away by the dielectric liquid. In order to generate small spark gaps, fine craters and to avoid idle pulses or short circuits, EDM machines, especially generator technology, have become very complex. EDM is also ideal for micro machining. In Figure 2.2, SEM photos of mechanically machined linear microchannel structures in different materials are shown (Brand *et al.*, 2006). The channels are about 200 μm wide and 70 μm deep.

- There are almost no process forces, electrode structures can be very simple (wire, shafts) which leads to filigree workpiece details with a high aspect ratio.
- All electrically conductive materials (steel, hard alloys, Ti, Pt, some ceramics, Si etc.) can be machined which is a good completion to other micro techniques.
- EDM is a 3D technique. Shape complexity can even be enlarged by combining die sinking, WEDM and other micro techniques like micro machining with Laser radiation, LIGA technology and dry as well as wet-chemical etching processes.

Currently, technological development of micro EDM turns out to be evolutionary rather than revolutionary. On the other hand, huge efforts are necessary to use Micro EDM techniques for industrial application, especially to fabricate complex tools and dies for the injection molding, embossing and punching of micro system components.

For efficient production, especially clamping, handling and in-situ-measurement systems should be developed. Due to the problems of optical vision control with pollution with debris or the dielectric liquid and with edge rounding, mechanically touching systems with micro balls may be integrated into EDM machines.

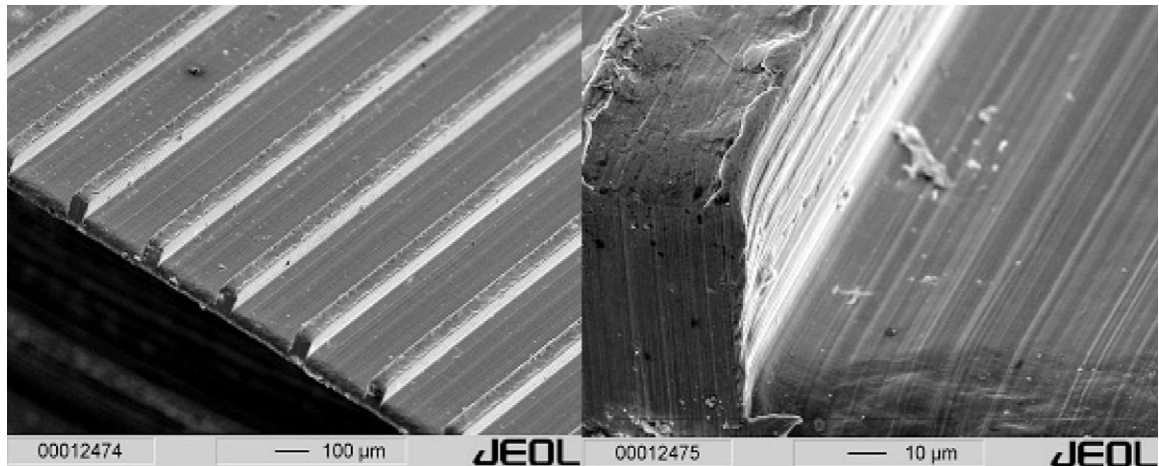


Figure 2.2. Left: SEM of linear microchannels in stainless steel, generated by mechanical micromachining. Right: SEM detail of the photo left.

2.4.2.1. Wire EDM machining (Electrical Discharge Machining). is an electro thermal production process in which a thin single-strand metal wire in conjunction with de-ionized water (used to conduct electricity) allows the wire to cut through metal by the use of heat from electrical sparks. Due to the inherent properties of the process, wire EDM can easily machine complex parts and precision components out of hard conductive materials.

2.4.3. Lamination

The fabrication techniques already discussed are important for the production of micro-channel reactors. However, lamination is an important and simple fabrication method for micro-channel reactors, the layering of numerous laminate sheets to produce a series of high aspect ratio micro-channels. Various metals have been employed and these offer very efficient heat and mass transfer during reaction processes and also significant pressure tolerance. The width of the channels is defined by the thickness of the laminates, while the machined area defines the length and height. Channel dimensions are in the order of 200 – 300 μm wide by 2000 – 5000 μm deep. The laminates may be joined by diffusion bonding, soldering, brazing or adhesive bonding techniques (Brand *et al.*, 2006).

2.5. Catalysts Coating Techniques

The range of reactions that could be performed in microstructured reactors would be seriously limited without combining heterogeneous catalysts with micro-channel reactor systems. Indeed, many of the applications for microstructured reactors reported employ catalysts located in micro-channels (Figure 2.3). There are a number of methods employed for addition of the catalyst, including the use of thin films of catalyst such as metals on the reactor wall, and supported catalysts packed into the channel. An alternative approach is to pack the catalyst in the micro-channel against an in situ-fabricated porous frit. Whatever method is used to immobilize the catalyst, it will prove to be important to appreciate that catalysts have different structures and that careful preparation and handling is vital.

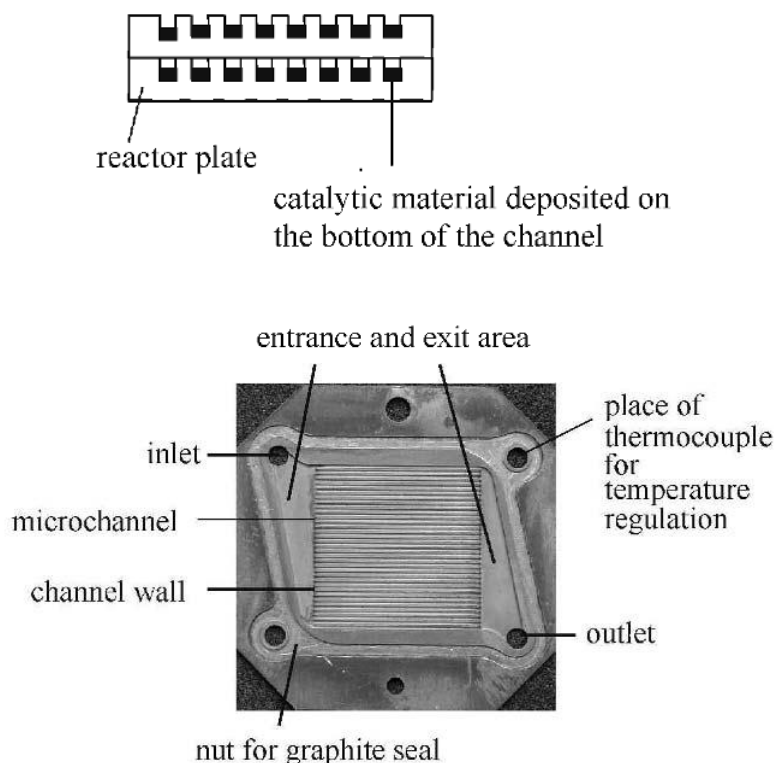


Figure 2.3. (a) Cross-section of two reactor plates; (b) photograph of a used stainless steel plate with deposited catalytic material (Steinfeldt *et al.*, 2003).

All of the microstructured reactor types for gas phase reactions require a solid catalyst to catalyze the gas phase reactions being carried out. Packed bed reactors are not the most efficient design as size is scaled down, due to large pressure drop, as predicted by the Ergun equation (Fogler, 1992). Also, channeling at the wall-particle interface becomes increasingly likely for creeping flow in microstructured reactors. If the packed bed catalyst sinters, there will be an increased pressure drop due to the reduction in the void fraction. One benefit of packed bed reactors is that commercial catalyst formulations that have already been optimized may be used.

Techniques to lower the overall pressure drop of catalytic microstructured reactors have been reported (Losey *et al.*, 2001, 2002) yet only a wall-coated channel geometry can eliminate the pressure drop due to form drag. The resulting pressure drop is controlled by the gas friction along the surface of the reactor, and in most cases is essentially negligible.

Advances in the technology of micro-structured catalytic reactors depend crucially on the catalyst layer development. Coatings need to be homogenous in thickness with a high surface area and an excellent adhesion as well as a good dispersion of the active phase and long-term stability. The deposition of catalysts in micro channels can be done by various means, the most prominent way being the wash-coat route followed by wet impregnation. Wash-coats constitute an accepted class of catalysts. Another class of industrially employed catalysts is created in micro reactors via the zeolite growth method (Wan *et al.*, 2002). Anodic oxidation is also widely used (Wiessmeier *et al.*, 1997) to generate nano-porous oxide support layers, when aluminum reactors can be employed. Besides this, thin-film techniques such as chemical vapor deposition CVD (Kestenbaum *et al.*, 2000) and physical vapor deposition (PVD), namely sputtering, serves for generating thin catalyst films. Furthermore, wall coating of catalysts can be done by a number of techniques ranging from dip and spin-coating to gas-assisted fluid displacement. The major limitation of the former is that these techniques can only be implemented on flat substrates prior to reactor assembly. Therefore, the challenge is to wall-coat non-porous micro-channels with catalyst slurries after reactor assembly.

In contrast VLSI (Very large scale integrated) manufacturing methods (PVD, CVD) provide alternative approaches for deposition of thin catalyst films, however these thin film deposition techniques may not provide the high surface area required for catalytic reactions and are restricted to elemental catalysts.

The generation of high surface areas in thin films includes anodic oxidation of silicon (Losey *et al.*, 2002) or aluminum (Wiessmeier and Honicke, 1996; Rebrov *et al.*, 2001; Wunsch *et al.*, 2002) surfaces through electrolysis or thermal oxidation of aluminum rich steel (Haas-Santo, *et al.*, 2001). These methods of creating porous structure are limited to submicron layers, and none of them are suitable for the methane steam reforming (MSR) reaction. Deposition of thin porous silica films through sol gel processing (Brinker, 1990; Zwinkels, 1996) has been done on flat or corrugated (Zhao *et al.*, 2002) substrates with the use of dip and spin coating methods. A major limitation is that dip and spin coating processes are limited to deposition of wash coats on carrier plates followed by reactor assembly. Although, this method is acceptable for laboratory studies it proves to be too costly for commercial devices used for portable power generation. Processes such as wall coating channels of millimeter dimension for monoliths used as catalytic converters in automobiles have been done for decades. However, the adhesion of the wash coat is known to be a function of substrate porosity. Methods of creating porosity on silicon, aluminum, and stainless steel surfaces have been used to prepare surfaces for wash coating of micro channels; nevertheless, these methods are manufacturing intensive.

Bravo *et.al.* (2004) has succeeded in properly incorporating a $\text{CuO/ZnO/Al}_2\text{O}_3$ methanol steam reforming catalyst for micro-channel reformers within a micro-channel. The existing packed-bed reactors are not an efficient design as a reactor size is scaled down because of large pressure drop. In addition, significant axial and radial temperature gradients can exist in the bed because of heat transfer limitations in a packed bed (Karim *et al.*, 2005). When the surface of the micro-channel is coated with the catalyst, the heat has to be transferred through channel walls and isothermal conditions can be achieved. In addition, the catalyst-coated micro-channel provides a lower pressure drop compared to granular catalyst packing inside the reactor.

Detailed descriptions of the procedures for the preparation of catalysts have, for instance, been given explicitly for wash-coats (Pfeifer *et al.*, 2005; Rouge *et al.*, 2001; Zapf *et al.*, 2003) and for zeolite growth (Wan *et al.*, 2002). Although comprehensive studies exist for the deposition of alumina coatings in monoliths (Nijhuis *et al.*, 2000) and on tubes and slabs (Valentini *et al.*, 2001), very few inclusive reports are devoted solely to catalyst/carrier coatings in micro channels, providing insight into the subject and a detailed characterization of the coatings in terms of preparation, morphology, porosity, composition. The latter paper evaluates the effect of a number of variables, i.e., initial particle size distribution, viscosity, nature and concentration of the binder and acidity, on the quality of catalyst coating in the case of open reactor systems, i.e., for a pre-coating procedure. Furthermore, Germani *et al.* (2007) performed a systematic study on the nature of binders used for coating a Cu/Zn/Al catalyst into micro-channels and their influence on catalytic activity for the water gas shift (WGS) reaction. They concluded that binders play a major role on (a) slurry viscosity by their chemical structure but also through their molecular weight, (b) coating adhesion and (c) catalytic activity by redispersion of the active phase because of metal complexes formation.

2.6. Assembling, Bonding and Packaging

Other issues in the microfabrication process are assembling, directly followed by the bonding process, packaging and sealing the devices to make them connectable to conventional process-engineering equipment. Some demands, difficulties and techniques for metal and polymer microstructure devices are briefly reviewed here.

While the assembling of a number of device parts is not really a problem in the macro-scale world, this step is more delicate to handle on the micro-scale. The main point is the adjustment and alignment accuracy of the parts, in addition to sealing, fixation and bonding technology problems. Depending on surface quality and the bonding technology applied, alignment errors may reach values similar in dimensions to the micro-structures themselves. An example is shown in Figure 2.4. Here, a number of microstructure foils with wet chemically etched micro-channels have been aligned to form fully elliptic channels. As seen in Figure 2.4, misalignment will lead to non-regular channels and therefore may interfere with the bonding technique. Correct alignment will lead to only

small deviations from the desired elliptical shape and the distortion during bonding will be small.

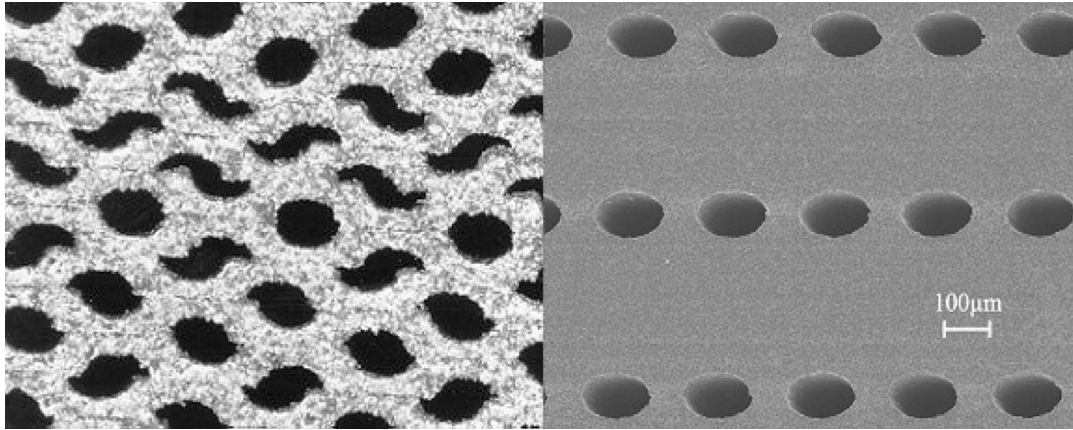


Figure 2.4. Left: Misalignment of microchannels. Right: correctly aligned microchannels forming full elliptical cross section.

A specialty of micro-structure assembling is directly correlated to the micro-structuring technology used. Burr formation on the top or at the sidewalls of the device structure does not play a major role in assembling macro-scale devices. In the micro-scale, burr formation generated by mechanical micromachining or laser machining may lead to significant problems with assembling of device parts as well as with the bonding. Thus, special attention has to be paid to burr microstructures or to avoid burr formation.

2.6.1. Metal Bonding

In most cases, it is not possible to manufacture microstructure devices from one part thus, they have to be assembled, eventually sealed and bonded together. Metals can be connected in various methods, e.g. by welding, soldering, screwing, compression, bolting, etc. The application of most of these techniques in building macro-devices is straightforward and has been well known for decades. However, in the connection of micro-structured devices special care has to be taken not to destroy the microstructure but still obtain a leak-tight seal. Hence, bonding techniques have to be adapted to meet the special demands of microstructure technology.

Microstructure devices are often made from metal foils. These foils are stacked, thereby obtaining passages. These passages have to be sealed against each other and against the environment. If there is one foil only, a straightforward way to seal the structure against the environment is to include the foil into an adapter using sealing such as O-rings or gaskets; this has been a standard method since the beginning of micro-structured flow devices. However, the use of gaskets or O-rings between foils is at least tedious, if not impossible. The alternative method is compression of foils by the external casing as demonstrated by IMM (Mainz Institute of Microtechnology) Mainz using graphite foils for sealing or compressing metal on metal; however, leak tightness is difficult to achieve due to roughness of the micro-structured platelets.

Most other methods of joining are non-removable, since they include alteration of the materials connected. These can be differentiated into techniques needing additional material to form the connecting layer, such as brazing, soldering and inter-metallic bonding, and those techniques where no other material is introduced, like electron-beam welding, laser welding and diffusion bonding. Conventional welding and soldering or all the other quite well-known techniques are not discussed here; but two processes are mentioned in particular: (a) diffusion bonding of metals and (b) laser micro-welding.

2.6.1.1. Diffusion Bonding. is a common process to generate microstructure devices to withstand high temperatures and high pressures and is therefore often used (Figure 2.5). Diffusion bonding is achieved by pressing a stack of metal foils in a controlled atmosphere at temperatures in excess of two-thirds of the melting temperature of the material for some hours (Brandner, 2008).

2.6.1.2. Laser Micro-Welding. gives very interesting opportunities that make a more precise description suitable, although laser welding may not be applicable for the joining of single foils. Two process strategies in laser welding are well established: laser deep penetration welding and laser conduction welding.

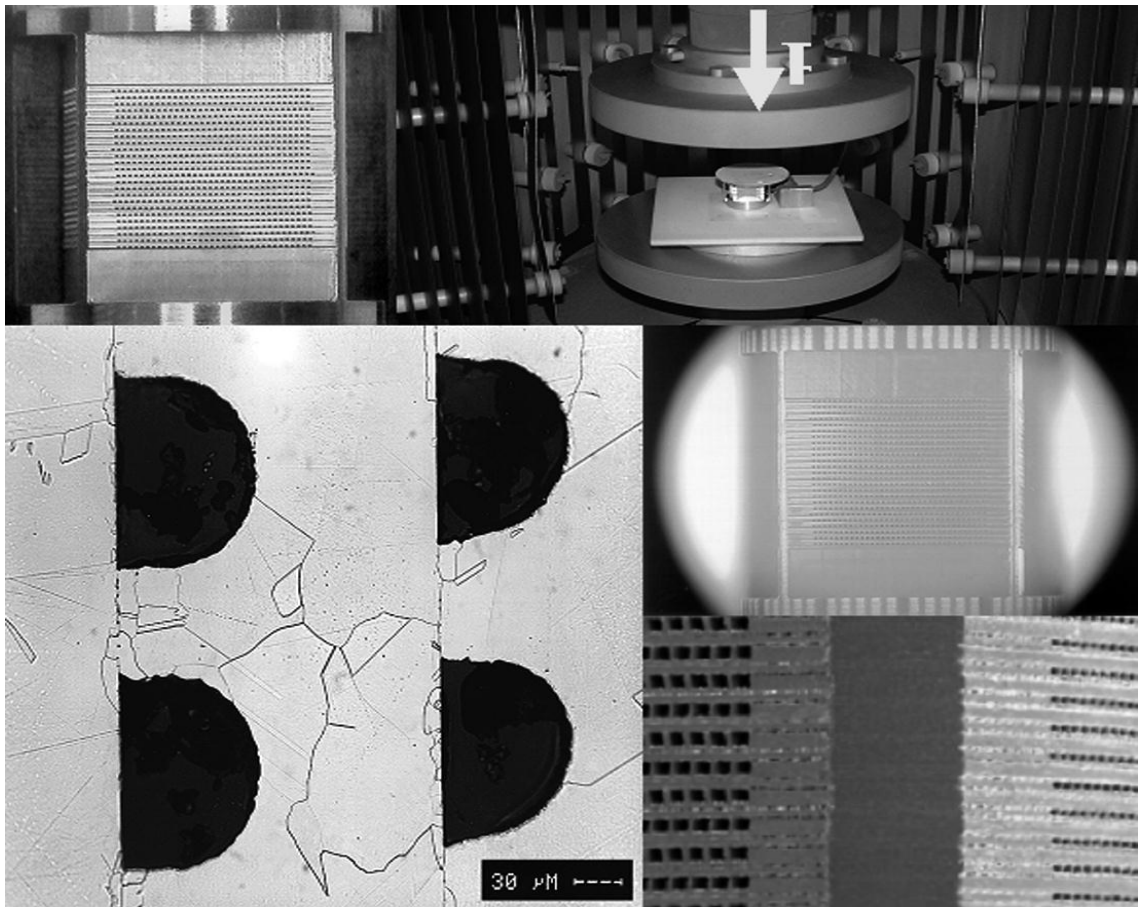


Figure 2.5. Diffusion bonding of microstructured metal foils. Clockwise: Stacked foils, diffusion bonding furnace, glowing device while bonding, generated channel system, boundary layer grain structure of diffusion-bonded microstructure foils.

2.7. Synthesis Gas Production in Microstructured Reactors

In recent years, the interest in portable fuel cell micro-power plants has increased significantly. Fuel cell micro-power plants provide an alternative for power generation in mobile devices such as cell phones, cameras and notebooks. Because of the high energetic efficiency of fuel cells, the energy density per volume and per weight of fuel cell systems is able to compete favorably with rechargeable batteries used in mobile devices today (Dyer, 2002; Rand and Dell, 2005).

2.7.1. Synthesis Gas Production from Methane

Due to the difficulty to store hydrogen in a microsystem, on-board hydrogen production by processing a hydrocarbon fuel is a preferred solution. Fuel cell micropowerplants have shown to be promising due to their high exergetic efficiency (Hotz *et al.*, 2006). A possible approach is the auto-thermal reforming of methane with steam and dry air to syngas consisting of hydrogen and carbon monoxide, which combines partial oxidation (POX), steam reforming (SR), and water gas shift reaction (WGS) reaction (Stutz and Poulikakos, 2005). The most important reactions in such a catalytic reformer are listed in Table 2.1 with their enthalpy of formation at standard conditions (Stutz *et al.*, 2006).

Stutz and Poulikakos (2008) investigated syngas (hydrogen and carbon monoxide) production by a numerical model of an adiabatic monolithic reformer (e.g. for a micro fuel cell system). Their study includes the thermal and diffusive properties of a washcoat of finite thickness that is modeled as a porous layer composed of a ceramic support containing catalytic active rhodium sites. It was combined with a two-dimensional radially symmetric model of a single tubular mini-channel, considering both the thermal and the diffusive transport phenomena in all domains. It was found that both the methane conversion and the hydrogen yield depended markedly on the washcoat thickness. An interesting result was obtained by implementing the common experimental conditions into the numerical model: if the inlet volume flow and the amount of catalyst per washcoat volume are constant, an optimum washcoat thickness of 70 μm was found, where the hydrogen yield is maximal. For a thinner washcoat, the smaller amount of catalyst is limiting, leading to a low methane conversion. For a thicker washcoat, the limiting effect is the reduced residence time, which stems inherently from the constraint of constant volume flow, rather than the increased diffusive resistance.

Various microstructured components for hydrogen production from methane have been presented by Pfeifer *et al.* (2005). Figure 2.7 shows a micro-scale methane reformer in which the steam reforming reaction was used to generate up to 500 W of power at a

temperature of ca. 1073 K and micro-scale system for generation of hydrogen by coupling the partial oxidation of propane with auto thermal reforming.

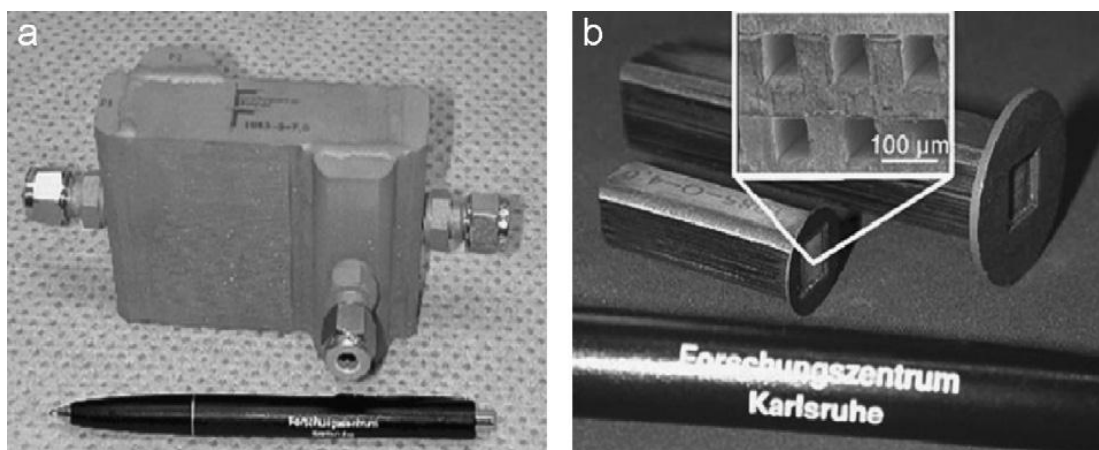


Figure 2.6. Microstructured systems for hydrogen generation by (a) methane reformer with a power output of 500 W, (b) coupling the partial oxidation of propane with auto thermal reforming.

Another micro-channel methane steam reforming reactor is presented with integrated catalytic partial oxidation of methane prior to catalytic combustion with low excess air (25%) to generate the required energy for endothermic methane steam reforming in adjacent channels by Tonkovich *et al.* (2004). Heat transfer rates from the exothermic reactions exceed 18 W/cm^2 of interplanar heat transfer surface area and exceed 65 W/cm^3 of total reaction volume for a methane steam reforming contact time near 4 ms. The process intensity of the presented methane steam reformer well exceeds that of conventional steam reformers, which have a typical volumetric heat flux below 1 W/cm^3 . The integration of multiple unit operations and improvements in process intensification result in significant capital and operating cost savings for commercial applications.

Table 2.2. Important mechanistic reactions inside the reformer and their enthalpy of formation at standard temperature and pressure.

Reactions		ΔH^0 (kJ·mol ⁻¹)
Partial oxidation (POX)	$\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	-35.7
Steam reforming (SR)	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	+206.1
CO generation (COG)	$\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$	-519.3
Water gas shift (WGS)	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-41.2
Total oxidation (TOX)	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-802.3
Oxidation of CO (OXCO)	$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	-172.5

Methane steam reforming (MSR) in catalytic microchannels was studied by a few research groups. The effect of the catalyst surface site density (catalyst amount) and reactor geometry on the reforming process of methane in a wall-coated, single-channel microreactor is investigated numerically by Stutz and his coworkers (Stutz *et al.*, 2006). It was found that the hydrogen selectivity changes significantly with varying catalyst loading due to the splitting rate of methane and water, which is a function of catalyst density. Furthermore, the study shows the significance of scaling the inlet volume flow not only with the reactor volume (gas space velocity) but also with the catalyst amount (catalyst space velocity). Another unexpected result was the presence of an optimum channel geometry and an optimum catalyst amount if the gas space velocity and the catalyst space velocity are constant. This underlined the necessity of coordinating the channel diameter, the inlet volume flow rate, and the catalyst amount in order to obtain a maximum reformer performance. Furthermore, it was necessary to specify the catalyst amount, the inlet conditions and the geometry in order to characterize sufficiently a catalytic reactor.

Highly active and coke-resistant Rh catalysts were developed for methane steam reforming in microchannel chemical reactors by Wang and his coworkers (Wang *et al.*, 2004). Rh loading was optimized on a stable MgO–Al₂O₃ support to improve the volumetric productivity for methane conversion. A 10 wt% Rh/MgO–Al₂O₃ catalyst into an engineered microchannel structure was integrated and H₂/CO ratios around 3.5, methane conversion and CO selectivity of ca. 60% and 80% were obtained, respectively. In particular, experimental results demonstrated that Rh/MgO–Al₂O₃ catalysts are extremely active for methane steam reforming and are resistant to coke formation at stoichiometric steam/carbon ratio of 1 for over 14 h time-on-stream with no sign of deactivation. Methane steam reforming activities on this catalyst were compared in both a microchannel reactor and a conventional micro-tubular reactor. Significant performance enhancement was observed in microchannel reactors owing to improved heat and mass transfer.

Ryu and his coworkers 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 (Ryu *et al.*, 2007). Compared with the same volume of coarsely powdered Ni catalysts, the monolith wash-coated Ni catalysts gave higher methane conversion in the steam reforming reaction, especially at gas hourly space velocities (GHSV) higher than 28000 h⁻¹, and with no pressure drop. A higher conversion of the monolith catalyst was obtained, even though it contains a lower amount of active catalyst (3 g versus 17 g for a powdered catalyst), which indicates that the heat-transfer capability of the wash-coated Ni catalyst is significantly enhanced by the use of a metal monolith. Testing the efficiency of the monolith catalyst using a shell-and-tube type heat-exchanger reactor with 912 cm³ of the monolith catalyst charged on to the tube side and hot combusted gas supplied to the shell side in a counter-current direction to the reactant flow, methane conversion greater than 94% was obtained at a GHSV of 7300 h⁻¹ and an average temperature of 913 K.

Another novel engineered, porous, ceramic, catalyst support for stable, high temperature (>1073 K) steam methane reforming operation was demonstrated with a rhodium catalyst by Johnson and his co-workers. They observed near equilibrium conversion and selectivity without catalyst deactivation at the reaction at high temperatures

(up to 1173 K), steam-to-carbon (S/C) molar ratio of 1.0, and a contact time of 27 ms. It was found that there was no degradation or sintering observed in the engineered, porous, ceramic support, the catalyst did not delaminate from the support, nor was any coke formation detected after 100 h time-on-stream (TOS) under these reaction conditions. (Johnson *et al.*, 2007).

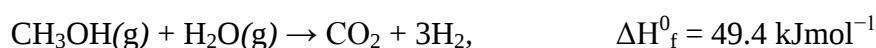
A demonstration pilot plant H_2 production at $5 \text{ Nm}^3\text{h}^{-1}$ in a microchannel system constructed using techniques proven in Heatric printed-circuit heat exchangers (PCHE) study was presented by Seris *et al.* (2008). The PCHE manufacturing technique is scalable and the results from this small-scale plant demonstrate not only a practical mini-plant for distributed manufacture of hydrogen but also provide the design basis for much larger plant (for example for transport fuelling and industrial applications) based on replication of the plate structures. Additionally, the system takes advantage of this to carry out the combustion and reforming reactions in highly integrated multiple adiabatic beds (MAB). The plant operated at 2 bar to produce hydrogen for a notional PEM fuel cell, with essentially complete conversion of natural gas in the reformer to equilibrium yields of CO, CO_2 and H_2 (~80%). The plant showed excellent turn-down characteristics to 30% of design capacity.

Wu *et al.* (2009) presented a study related to a monolith catalysts with different Ni contents (5, 10 and 15 wt%) as well as 10% Ni/ $Ce_xZr_{1-x}O_2$ /SBA-15/ Al_2O_3 /FeCrAl ($x=0$, 0.5 and 1) metal monolith catalysts with $Ce_xZr_{1-x}O_2$ of 1.7 wt% to test the catalytic activity and stability of these catalysts for steam reforming of methane. They indicated that Ni/SBA-15/ Al_2O_3 /FeCrAl metal monolith catalysts with Ni loading above 10 wt% had good catalytic activities under atmospheric pressure. For 10% Ni/ $Ce_xZr_{1-x}O_2$ /SBA-15/ Al_2O_3 /FeCrAl ($x=0$, 0.5 and 1) metal monolith catalysts, CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ as promoters can improve the activity and stability of metal monolith catalysts, while the addition of ZrO_2 can lead to the decrease of catalytic activity and stability. The 10% Ni/ $Ce_{0.5}Zr_{0.5}O_2$ /SBA-15/ Al_2O_3 /FeCrAl metal monolith catalyst exhibited excellent activity and stability at 1073 K for 110 h on stream. The activity of 10% Ni/SBA-15/ Al_2O_3 /FeCrAl metal monolith catalyst gradually decreased at 1073 K after 60 h on stream. The reason for this phenomenon is probably the formation of $NiAl_2O_4$ on the surface of catalyst.

2.7.2. Synthesis Gas Production from Methanol

Methanol has many advantages over other liquid fuels as a hydrogen source (Yong *et al.*, 2004; Lindstrom and Pettersson, 2001; Delsman *et al.*, 2006). The cracking temperature of methanol (~523 K) is low compared to other fuels, which decreases CO emission that poisons the PEMFC anode electro-catalyst. The boiling temperature of methanol is fairly low and heat input for evaporation is low as a result. In addition, methanol can be safely dealt with and stored easily because it is liquefiable at a moderate pressure. Due to the high H/C ratio in the fuel, soot formation is significantly lower than other liquid hydrocarbons.

Catalytic steam reforming of methanol has been performed successfully in macro scale devices. The reforming process, expressed in the chemical equation below, is mildly endothermic:



The reaction produces 3 moles of hydrogen and 1 mole of CO₂ per mole of methanol on a dry basis. Trace species including CO and CH₄ are also formed. CO formation is particularly important as CO is strongly poisonous to Pt catalyst of the fuel cell (Holladay *et al.*, 2004). As the reforming process is endothermic, the heat and mass transfer inside the catalytic reactor is important. If the temperature distribution within the reactor is unfavorable, the reaction rate decreases or undesired species can be produced (Nagano *et al.*, 2001). A multi-passage microchannel type reactor was selected for the reforming reactor, as it has many advantages such as enhanced heat and mass transfer, the flow uniformity as well as the surface-to-volume ratio can be maximized in this configuration while maintaining the overall reactor volume small (Park 2005; Kolb and Hessel, 2004).

Recently, many efforts concerning micro-structured reactors for catalytic reactions have been reported (Kiwi-Minsker and Renken, 2005; Kolb and Hessel, 2004) Many

researchers have developed the catalytic micro-structured reactor for steam reforming of methanol. Holladay *et al.* reported a micro scale fuel reformer for a sub-watt power generation system (Holladay and Jones, 2002; Holladay *et al.*, 2004). Reuse *et al.* (2004) fabricated and tested the methanol steam reformer and methanol combustor using a micro-structured stainless steel plate. Park *et al.* (2005) developed an integrated micro-channel fuel processor using also a stainless steel sheet by wet chemical etching. In addition, micro-structured reactors for hydrogen production using MEMS technology have been reported. Pattekar *et al.* (2004) fabricated and tested a silicon-chip based micro-structured reactor showing performance enough to supply hydrogen to a 9.48 W fuel cell. CASIO reported a glass multi-layered micro-structured reactor with a methanol reformer (Terazaki *et al.*, 2005). In another study, Taegyu Kim and Sejin Kwon (2006) have fabricated and tested a catalytic micro-structured reactor for hydrogen production; and Cu/ZnO catalyst was selected for methanol steam reforming.

Besides the parallel multi-channel reactor, it is possible to see micro channel reactors in various geometries. Micro-structured string-reactor designed as catalytically active wires placed in parallel into a tube was developed by Horny *et al.* (2004). String-reactor which has a small diameter of the channels ($<100\text{ }\mu\text{m}$) provides a narrow residence time distribution (RTD), a low pressure drop and a short radial diffusion time. The reactor was used for hydrogen production from methanol with autothermal reforming over Cu/ZnO/Al₂O₃ catalyst observing CO₂ selectivity of 99% and H₂ selectivity of 60%.

Micro-channels of silicon-based micro-reactors were successfully coated with Cu–ZnO–Al₂O₃ catalyst by a fill-and-dry coating method, applicable to pre-assembled micro-reactors, for steam reforming of methanol (Hwang *et al.*, 2007). The 10–20 μm thick catalyst layers could be formed on the inner walls of the micro-channels after the micro-channels were fully filled with catalyst slurry. The highest catalytic activity without loss of intrinsic catalytic activity was obtained using 1:5 (catalyst to solvent) DI water-based catalyst layers coated by fill-and-dry coating. The maximum H₂ production rate was 85 cm³ with 1650 ppm of CO measured at 573 K using a methanol feed rate of 9 cm³/h.

Steam reforming of methanol was performed in one stainless steel micro-channel reactor coated with commercial catalyst by Kundu and his coworkers (Kundu *et al.*, 2007). The different sols (alumina, zirconia and mixed sol of alumina and zirconia) as a binder for the catalyst were applied to compare the stability and performance. Among the different sols, mixed sol of alumina and zirconia comparatively produced better stability and performance.

Chen *et al.* (2007) reported that the wall coated catalysts in a microchannel reactor for methanol oxidation reforming. The preparation method of the wall coating catalyst was studied in detail, i.e., the sol-gel and solution-coating techniques. To prepare the catalysts for methanol oxidation reforming, the washing-coating layer of CuZnAl was prepared by the sol-gel technique, and then the active layer was coated on it by solution-coating technique with emulsion colloid containing Pd-ZnO particles. The catalyst prepared has high activity and relatively high stability. A numerical simulation of methanol steam reforming in a microreactor integrated with a methanol micro-combustor was presented by Tadbir and Akbari (2011). Typical Cu/ZnO/Al₂O₃ and Pt catalysts were considered for the steam reforming and combustor channels respectively. Effects of Cu/ZnO catalyst thickness, gas hourly space velocities of both of steam reforming and combustion channels, reactor geometry, separating substrate properties, as well as inlet composition of the steam reforming channel were investigated. Results indicated that increasing catalyst thickness would enhance hydrogen production by about 68% when the catalyst thickness is increased from 10 μm to 100 μm . Gas space velocity of the steam reforming channel shows an optimum value of 3000 h^{-1} for hydrogen yield, and the optimum value for the space velocity of the combustor channel is calculated at 24000 h^{-1} . The produced hydrogen from an assembly of such microreactor at optimal conditions will be sufficient to operate a low-power, portable fuel cell.

The performance of different Cu/CeO₂/Al₂O₃ catalysts of varying compositions was investigated for OSR of methanol in order to produce the hydrogen selectively for PEMFC applications by Patel and Pant (2007). The effect of various operating parameters was studied are as follows: reaction temperature, contact time and oxygen to methanol (O/M) molar ratio. Catalyst Cu-Ce-Al: 30-20-50 exhibited 100% methanol conversion and 179

$\text{mmol}\cdot\text{s}^{-1}\cdot\text{kg}\cdot\text{cat}^{-1}$ hydrogen production rate at 553 K with carbon monoxide formation as low as 0.19%. The high catalytic activity and hydrogen selectivity shown by ceria promoted $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts is attributed to the improved specific surface area, dispersion and reducibility of copper which were confirmed by characterizing the catalysts through temperature programmed reduction (TPR), CO chemisorption, X-ray diffraction (XRD) and N_2 adsorption–desorption studies.

Production of hydrogen with partial oxidation of methanol (POM) ($\text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow 2\text{H}_2 + \text{CO}_2$) was investigated by Chang *et al.* (2008) over $\text{Au}/\text{Al}_2\text{O}_3$ and ZnO promoted $\text{Au}/\text{Al}_2\text{O}_3$ ($\text{Au}/\text{ZnO}/\text{Al}_2\text{O}_3$) catalysts. The addition of ZnO to $\text{Au}/\text{Al}_2\text{O}_3$ resulted in higher catalytic activity for POM to produce hydrogen. The activity of the catalyst for hydrogen formation increases with increasing the addition of ZnO, and it reaches a maximum when the atomic ratio of Zn to Au is 5/1. The main role of ZnO is associated with the progressive formation of smaller Au particles, which comprise active oxygen species for oxidation of methanol. Catalytic activity of $\text{Au}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst at various calcination temperatures shows that the uncalcined sample exhibits higher activity for hydrogen formation.

2.7.3. Synthesis Gas production from other Hydrocarbons

Hydrogen can be obtained from hydrocarbons other than methane and methanol, such as diesel, gasoline and higher alkenes. Hu *et al.* (2003) reported that more than 95% conversion can be achieved by steam reforming of clean fuels, such as isooctane and synthetic diesel.

A study of hydrogen production by gas phase partial oxidation of toluene over V/Ti oxide catalysts has been successfully performed in a micro-channel reactor (Hao *et al.*, 2005) which provides very good mass and heat transfer conditions. With the elimination of hot spots, which are known as the most negative factors in partial oxidation of hydrocarbons, steady and uniform reaction conditions can be achieved in the catalyst bed by using the microreactor. Since the best performance of the catalysts might be exploited,

the selectivity of partial oxidation products of toluene has remarkably increased compared to the traditional packed fixed-bed reactor, even without modifying the catalysts, diluting the reactants or catalysts with inert contents to avoid hot spots or to improve the diffusion and mixing. Using TiO_2 carrier with 5% V_2O_5 loading as catalyst, the total selectivity of benzaldehyde and benzoic acid reaches around 60%, and the toluene conversion is about 10%.

Rh impregnated Al_2O_3 on Fecralloy microchanneled reactor was studied in partial oxidation (POX) and oxidative steam reforming (OSR) reactions for production of hydrogen or synthesis gas from propane by Aartun *et al.* (2005). Temperature profiles obtained along the reactor axis show that the metallic microchannel reactor is able to minimize temperature gradients due to exothermal reactions. The Rh/ Al_2O_3 /Fecralloy microchannel reactor also shows good stability during more than 70 experiments of both POX and OSR with temperature cycling from 573 to 1273 K. However, it is reported that at sufficiently high furnace temperature, the gas phase in front of the Rh/ Al_2O_3 /Fecralloy microchannel reactor ignites leading to lower syngas formation and higher selectivity to total oxidation products and hydrocarbon by-products. Another OSR of propane study for hydrogen production over Pt/ CeO_2 catalyst in monolithic, packed-bed and jellyroy reactor was performed to produce hydrogen by Vita *et al.* (2010). The structure with circular concentric design as a “jellyroll” exhibited better performance in terms of fuel conversion, hydrogen production and low by-products formation coupled with an economy of the catalyst of about to 43% with respect to the traditional packed bed system.

2.7.4. Catalysts

Compared with the precious metal catalysts such as Rh-based ones, Ni based catalyst are currently being used in the commercial steam-reforming processes due to the fact that they are cheaper but still offer sufficient activity (Rostrup-Nielsen, 1984; Trimm and Önsan, 2001). Although Rh-based catalysts are more expensive, they offer higher activities than Ni-based ones, as well almost no carbon formation. Coke formation is a challenging issue during steam reforming over Ni-based catalyst, but can be minimized by robust control of the operating conditions such as the steam-to-carbon ratio. It is reported that, this

ratio that changes with the type of hydrocarbon should not be below ca. 2.5 during steam reforming of methane over Ni-based catalysts (Rostrup-Nielsen, 1984; Trimm and Önsan, 2001; Avcı *et al.*, 2002). Supports used also have a crucial role in coke formation. It is reported that magnesia or potassium, both of which are alkaline components, eliminates coke formation (Ross, 1974). Steam reforming activities of supports varies in the order of $\text{Ni/TiO}_2 > \text{Ni/C} > \text{Ni/SiO}_2 > \text{Ni/MgO}$ (Bradford and Vannice, 1996).

Avcı (2003) reported that the specific activities of several metals doped on alumina or magnesia are in the order of $\text{Rh, Ru} > \text{Ni, Pd, Pt} > \text{Re} > \text{Co}$. Oxidation reaction of methane which is the most stable hydrocarbon can be achieved on challenging conditions. Among the precious metals such as Platinum and Palladium, mostly, palladium based catalysts are preferred, since light-off temperature of methane oxidation is the lowest for this choice (Ciaparu and Pfefferle, 2001). Additionally, rhodium-based (Burch *et al.*, 1999), and platinum-based (Michalkiewicz 2006; Ma *et al.*, 1996) catalysts are being utilized. Light-off temperature is another characteristic of total oxidation (TOX) and depends on the hydrocarbon/oxygen ratio (Veser and Schmidt 1996). Ma *et al.* (1996) reported that as methane/oxygen ratio increases, light-off temperature decreases. Avcı and co-workers (2003) have studied the relation between light-off temperatures and fuel/oxygen ratio. Relation between the fuel/oxygen ratio and minimum light-off temperatures relation between n-butane and propane reacting on Pt-Ni catalyst has been explained by the possible interaction between two sites (Avcı *et al.*, 2003).

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

The gases and chemicals used in the study were all research grade. The suppliers of chemicals used for catalyst preparation and their specifications are given in Table 3.1.

Table 3.1. Chemicals for catalysts preparation.

Chemical	Specification	Source	Molecular weight
Nickel (II) nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 20.18% Ni	Sigma-Aldrich	290.81
Tetraammineplatinum(II) nitrate	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ 50.4% Pt	Sigma-Aldrich	387.22
Ru (III) nitrosyl nitrate solution	$\text{Ru}(\text{NO})(\text{NO}_3)_3$ 1.5% Ru	Sigma-Aldrich	318.10
Rh (III) nitrate solution	$\text{Rh}(\text{NO}_3)_3$ 10% Rh	Sigma-Aldrich	288.92
Palladium (II) nitrate dihydrate	$\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ 39.53% Pd	Sigma-Aldrich	266.46
Gamma alumina	$\gamma\text{-Al}_2\text{O}_3$	Alcoa	-

3.1.2. Gases

All of the gases used in this research (Table 3.2) were supplied by Birleşik Oksijen Sanayi (BOS) and HABAŞ Companies, Istanbul, Turkey.

Table 3.2. Specifications and applications of the gases used.

Gas	Specification	Application
Hydrogen	99.99 % (BOS)	GC calibration, Reduction
Carbon Dioxide	99.999 % (BOS)	GC calibration, reactant
Carbon Monoxide	99.999 % (BOS)	GC calibration
Helium	99.999 % (BOS)	GC carrier gas
Nitrogen	99.998 % (BOS)	Inert
Dry Air	78.4 % N ₂ + 21.5 % O ₂ (BOS)	GC calibration
Methane	99.9 % (BOS)	GC calibration, Reactant
Argon	99.999 % (BOS)	GC carrier gas

3.2. Experimental Setup

The experimental systems used can be divided into four groups:

- **Catalyst Preparation Systems:** The set-ups used for catalyst support preparation as well as incipient-to-wetness impregnation of active metals are included in this group of experimental systems.
- **Catalyst Characterization Systems:** This group involves three different analytical and spectroscopic techniques which are used for catalyst characterization to determine the physical and microstructural properties of the catalyst samples prepared and to examine the changes during and/or after reduction or reaction.
- **Catalytic Reaction System:** The continuous flow microreactor system includes gas and liquid flow control, temperature controlled transfer lines, gas/liquid mixing,

temperature controlled reaction chamber, and feed and product sampling sections. This system is used for determining catalytic activity, selectivity and stability.

- **Product Analysis System:** Quantitative determination of the composition of the species, both in the reactor effluent and in the feed stream, is conducted by two gas chromatographs that are connected on-line to the microreactor flow system.

3.2.1. Catalyst Preparation Systems

The experimental system used for preparing particulate catalysts by incipient-to-wetness impregnation technique (Figure 3.1) includes a Retsch UR1 ultrasonic mixer, a vacuum pump, a Büchner flask and a MasterFlex computerized-drive peristaltic pump.

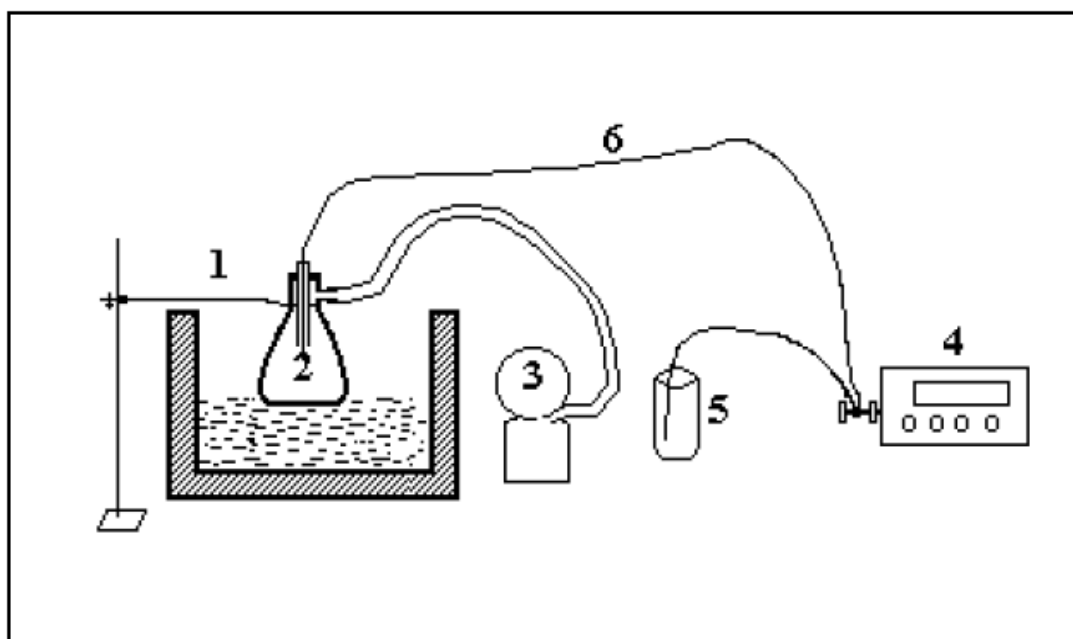


Figure 3.1. Schematic diagram of the impregnation system (Akin, 1996). (1. Ultrasonic mixer, 2. Büchner flask, 3. Vacuum pump, 4. Peristaltic pump, 5. Reactant storage tank, 6. Silicone tubing).

3.2.2. Catalyst Characterization Systems

3.2.2.1. Scanning Electron Microscopy (SEM). Micrographs of the fresh and reduced catalyst samples as well as the support materials were taken using an environmental scanning electronic microscope (ESEM), to observe the morphology differences. X-ray analytical mapping and Energy Dispersive X-Ray Spectroscopy (EDS) tests were also conducted on catalyst samples in order to clarify their elemental analysis and to obtain information on the dispersion of the metals on the catalyst surface. The tests were conducted in a Philips XL 30 ESEM-FEG system, having a maximum resolution of 2 nm. The experiments were performed at the Advanced Technologies Research and Development Center of Bogaziçi University.

3.2.2.2. High Resolution Transmission Electron Microscopy (HRTEM). To obtain information on the surface morphology variation of the reduced catalyst samples, HR-TEM analyses were carried out using TEKNAI G² F20 S-TWIN HRTEM operating at 200 kV. The analyses were performed at Gebze Institute of Technology by Ömer Faruk Deniz.

3.2.2.3. X-Ray Diffraction (XRD). The crystalline phases of the catalyst samples and their particle sizes were identified by using a Rigaku D/MAX-Ultima+/PC X-Ray diffraction equipment having an X-ray generator with Cu target and scan speed of 2 °/min. The experiments were performed at the Advanced Technologies Research and Development Center of Bogaziçi University.

3.2.2.4. HSC-Chemistry Software. The equilibrium calculations for MSR and water gas shift reactions were conducted using HSC-Chemistry 4.1; the effect of different reactants, feed compositions and temperature on the product composition was determined.

3.2.3. Catalytic Reaction System for SMR and OSR of Methane

The catalytic microreaction system shown in Figure 3.2 was designed and constructed in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department, Bogaziçi University and involved three distinct sections for feed adjustment, catalytic reaction and product analysis.

1/4", 1/8" and 1/16" OD stainless steel or brass tubing, valves and fittings for feeding liquid water and gaseous species were used in the system. The flow rates of research grade high purity gases (methane, nitrogen, hydrogen, carbon dioxide, carbon monoxide) from pressurized cylinders passed through the system were controlled by Omega Model 5878 digital mass flow controllers of which set values were adjusted by the main control unit. Mass flow controllers were calibrated for each gas and calibration curves are given in Appendix A. All gases, after being mixed, were sent into the reaction section which consists of a 10 mm ID quartz fixed-bed down-flow reactor (Figure 3.3), for conventional packed bed experiments, or a 20 mm ID quartz fixed bed tube into which a cylindrical engineered metal housing made of 310-grade stainless steel with external dimensions of 18.6 mm $\times$ 30 mm (outer diameter $\times$ length) was fitted for microchannel reactor experiments. The details of the microchannel reactor design are presented in Section 3.4.4. Quartz tubes were connected with two custom design fittings to the 1/4" stainless steel main line. The total length of the reactor was 80 cm, which is longer than the furnace tube so that the fittings of the reactor can be kept out of the furnace to facilitate manipulation during catalyst charging or recharging. Position of the tube center and hence of catalytic zone are adjusted to remain within the 100 mm long constant temperature zone of a 30 mm ID $\times$ 600 mm tube furnace. The tube furnace was controlled and measured to ± 0.1 K by a Shimaden FP-21 programmable temperature controller and a K-type sheathed thermocouple, the latter being placed in the center of the furnace adjacent to the microchannels. Ceramic wool was used to hold the catalyst bed in fixed position. Ceramic wool was also placed at the top and the bottom ends of the furnace to prevent heat loss for maintaining a stable reaction temperature. In the reactant and product sampling section, the reactant mixture entering or the product leaving the reactor were passed through two ON-OFF valves to either the GC sampling unit which has a calibrated one milliliter sample loop for analysis or to the soap bubblemeter for measuring the flow rate of the effluent at the ambient temperature.

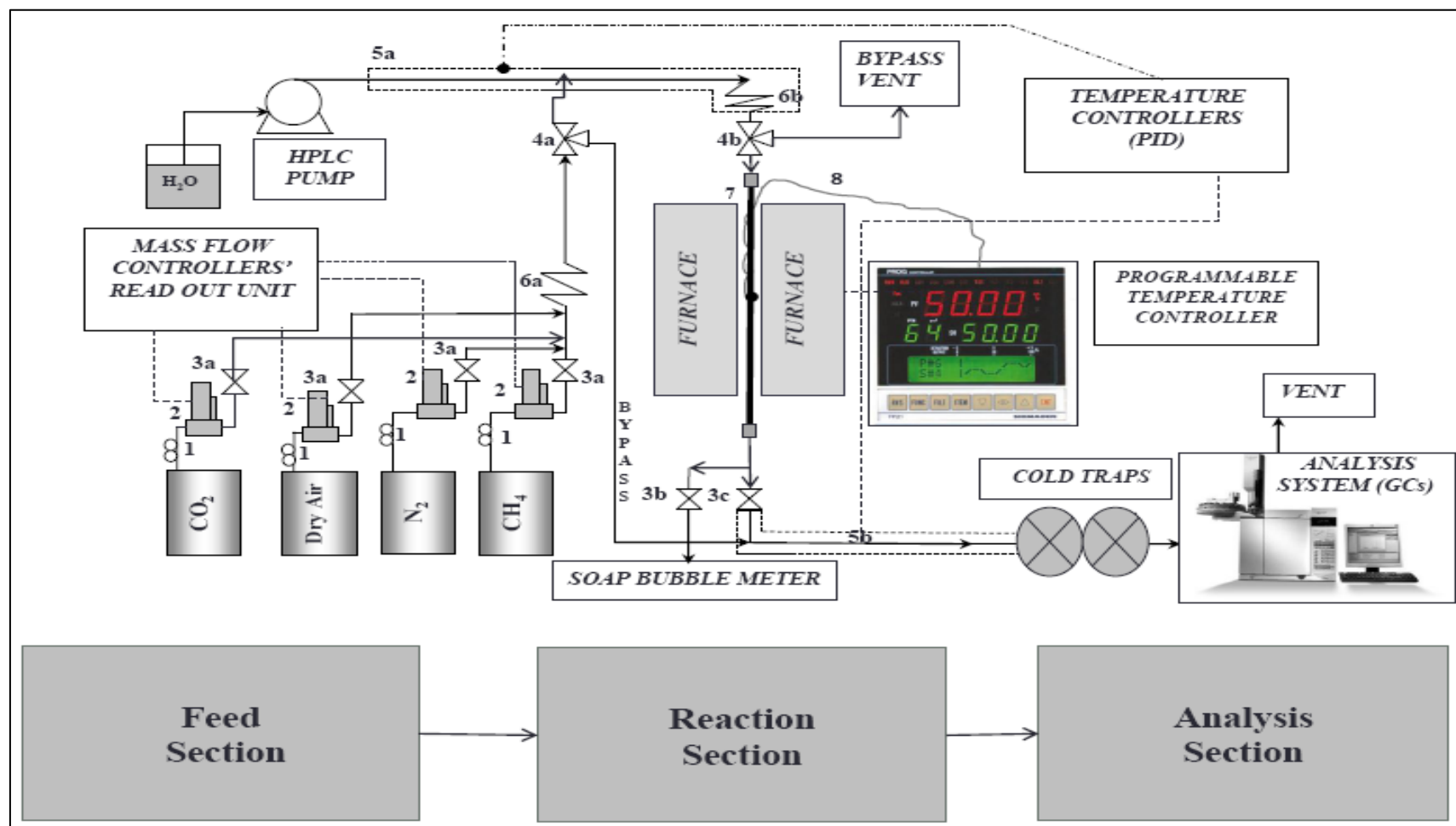


Figure 3.2. Schematic diagram of the microreactor flow system (1. Gas tank and regulator, 2. Mass flow controller 3. On-off valve, 4. Three-way valve, 5. Heated zone, 6. Mixing zone, 7. Microchannel reactor in furnace, 8. K type thermocouple).

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. In order to feed water in the form of steam, the 1/16" stainless steel tubing through which water was allowed to flow, and the line going to reactor after the on-off valve including the reactant mixing zone, were kept at 398 ± 5 K using a 1 m Cole-Parmer heating tape, a 16-gauge wire K type sheathed thermocouple and temperature controller. The heating tape was covered with ceramic wool insulation to prevent heat losses.



Figure 3.3. 10 mm ID quartz fixed-bed down-flow reactor.

3.2.4. Product Analysis System

In the first, second and third stages of the experiments, the product mixture containing unreacted methane and permanent gases involving hydrogen, oxygen, nitrogen, and others involving carbon monoxide, carbon dioxide and water were analyzed with Analysis Set 1 (Figure 3.4). Considering that all these species excluding water were needed to be analyzed quantitatively, use of two different gas chromatographs was essential; hydrocarbons were effectively analyzed using a Porapak Q column with helium carrier gas whereas quantitative detection of hydrogen and other fixed gases were analyzed using a Molecular Sieve column with argon carrier. A Shimadzu GC-14A gas chromatograph equipped with a Thermal Conductivity Detector (TCD) was used to analyze methane and carbon dioxide. In order to analyze fixed gases, hydrogen, carbon monoxide and methane, a Shimadzu GC-8A gas chromatograph equipped with a Thermal Conductivity Detector

(TCD) involving a Molecular Sieve (MS) column was employed. Analysis conditions are given in Table 3.3. Additionally, columns were conditioned before use at 523 K overnight to ensure removal of possible impurities on packing materials. Before proceeding with the reaction experiments, the gas chromatographs were calibrated by known values of the species to be analyzed under the conditions given in Table 3.4 and by reading the area under the peak calculated by the computer software. Using this procedure, mole versus peak area curves were constructed for each gas and the corresponding calibration factors were determined by linear regression.

Table 3.3. Analysis Sets.

	Analysis Set 1		Analysis Set 2
GC Parameter	A Shimadzu GC-14A	Shimadzu GC-8A	A Shimadzu GC-14
Detector type	TCD	TCD	TCD
Column temperature, K	363	333	50-150
Injector Temperature, K	423	363	383
Detector Temperature	423	363	443
Detector Current, A	120	60	60
Carrier Gas	Helium	Argon	Argon
Carrier Gas Flow Rate, cm ³ /min	25	50	25
Column Packing Material	Porapak Q, 80-100 mesh	Molecular Sieve 5A, 60-80 mesh	Carboxen 1000, 80-60 mesh
Column Tubing Material	Stainless Steel	Stainless Steel	Copper
Column Length & ID	300 x 3 mm	200 x 2 mm	210 x 3 mm
Sample loop	1 cm ³	1 cm ³	1 cm ³

In the fourth stage of the experiments, the product mixture with unreacted methane and permanent gases including hydrogen, oxygen, nitrogen, carbon monoxide, and carbon dioxide (except water) were analyzed with Analysis Set 2 (Table 3.3). Considering that all these species excluding water were needed to be analyzed quantitatively, the system was modified to analyze all gases in a single GC using Carboxen 1000 packed column in Shimadzu GC-14A. As in the case of Analysis Set 1 instruments, Analysis Set 2 instrument (Shimadzu GC-14A) were conditioned and calibrated again for each species. A temperature program (Figure 3.5) was applied for effective separation and analysis of the gases.

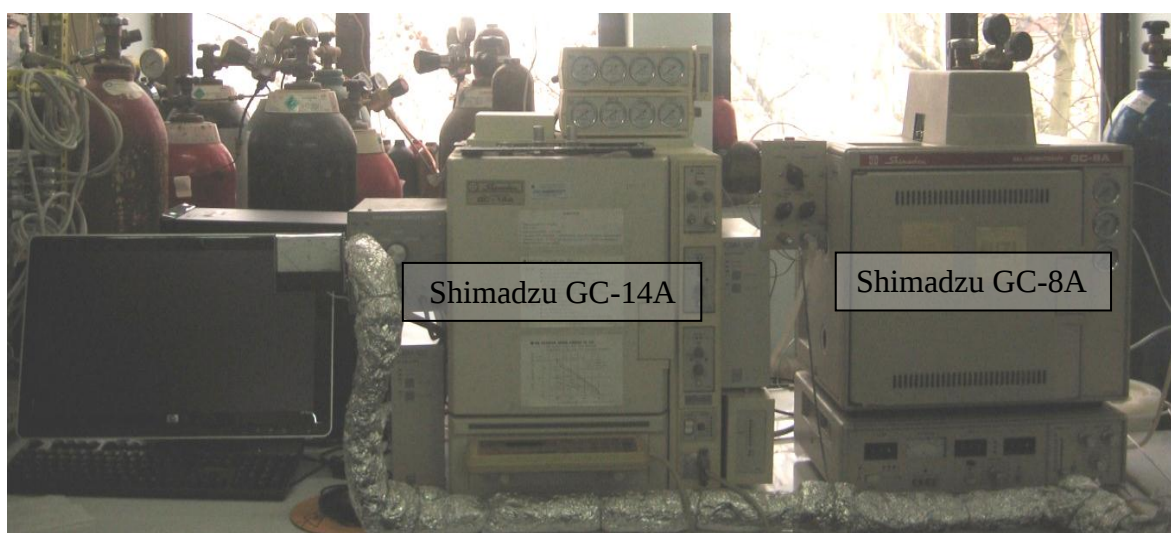


Figure 3.4. Analysis Set 1: Two Shimadzu gas chromatographs.

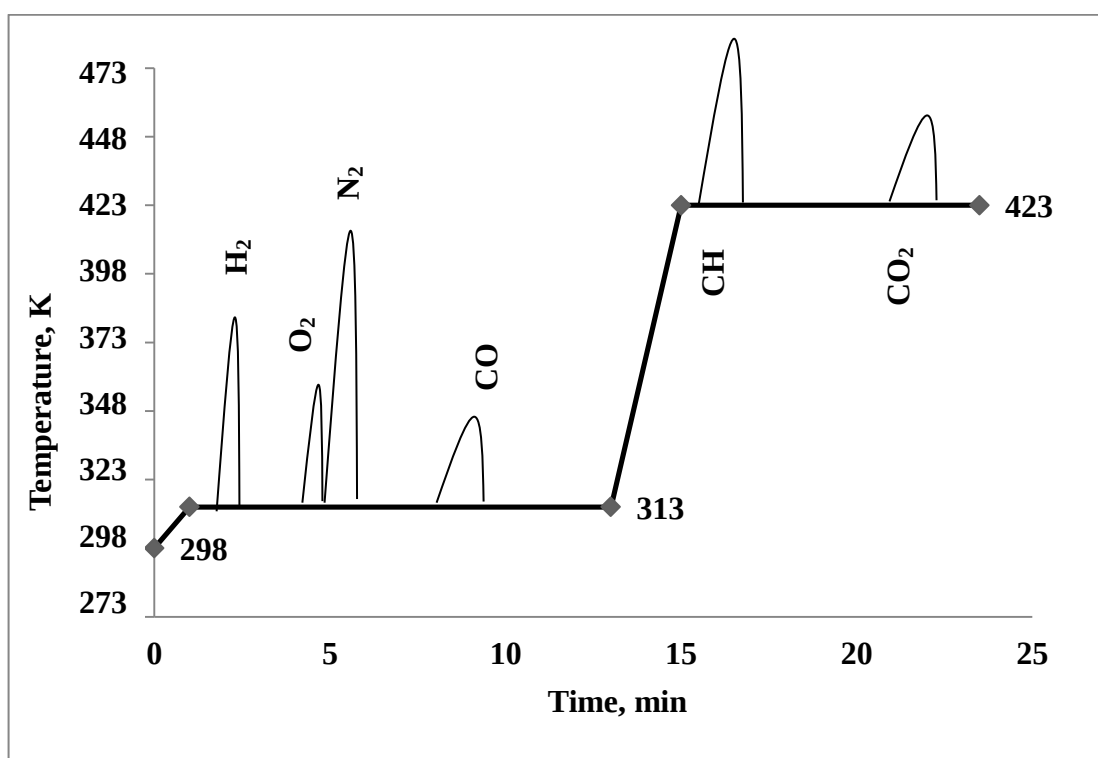


Figure 3.5. Temperature program used for the GC oven (column) in OSR experiments.

3.3. Catalyst Preparation and Pretreatment

In the scope of this thesis, according to the active metal(s) used, six different sets of catalysts were prepared, characterized and tested in conventional packed bed microreactor and/or in packed or coated microchannel reactors. The difference between the catalysts used for conventional packed bed (CPB) and microchannel reactors (MCR) is the particle size of the support and the additional coating procedure for MCR catalysts.

- Ni/ δ -Al₂O₃
- Pt-Ni/ δ -Al₂O₃
- Pt/ δ -Al₂O₃
- Rh/ δ -Al₂O₃
- Ru/ δ -Al₂O₃
- Pd/ δ -Al₂O₃

The preparation procedure of each catalyst sample is explained in detail below. In order to obtain high catalytic activities, a pretreatment involving the reduction of the active metals from their oxide state – which was formed during the calcinations- to their metallic state was required prior to the reaction, since catalysts in their oxide forms are usually inactive in catalyzing the MSR and OSR reactions. The details of this procedure are given in Section 3.3.2.

3.3.1. δ - Al_2O_3 Support Preparation

The catalytic MSR and OSR of methane are known to be high temperature reactions. Therefore, all catalyst supports used in the scope of this work should not only have high surface areas but also show high thermal stability. γ - Al_2O_3 is commonly used support material owing to its high surface area. However, it does not have thermal stability at temperatures higher than 900 K and tends to be open to carbon formation in the presence of steam. The alumina support which has high surface area and is thermally stable in the high reaction temperature region can be obtained by conducting thermal treatment. The thermal treatment applied to γ - Al_2O_3 is specified in Table 3.3. Avci (2003) reported that the support material prepared in 45-60 mesh size by this procedure has $81.6 \text{ m}^2 \cdot \text{g}^{-1}$ surface area and is named as δ - Al_2O_3 . δ - Al_2O_3 was used as support for all catalysts prepared for testing packed and microchannel reactor designs. Particle sizes of the support for the catalyst used varies in different experiments vary in the range of 10-18 to 60-80 mesh.

Table 3.4. Support preparation procedure.

Crushing γ - Al_2O_3 pellets with 3 mm particle size
Sieving of γ - Al_2O_3 to obtain particles in desired mesh sizes (10-18, 30-45, 45-60, 60-80, etc.)
Drying of γ - Al_2O_3 at 423 K for 2 h
Calcination of γ - Al_2O_3 particles at 1173 K for 4 h

3.3.2. Particulate Catalyst Preparation and Pretreatment

All monometallic δ - Al_2O_3 supported catalysts were prepared by the incipient to wetness impregnation technique using precursor salts that are given in Table 3.2. Equivalent of 15% by weight nickel metal was loaded on the support. The loadings of precious metal catalysts were the equivalent of 2% by weight metal. In each case, the precursor salts were dissolved in a defined amount of distilled water (ca. 1 cm³ solution / g support). The support in desired particle size, δ - Al_2O_3 , was put into the Buchner flask and mixed ultrasonically for 25 minutes under vacuum. The aqueous solution of the precursor salts were impregnated on the support using a peristaltic pump. The slurries obtained were ultrasonically mixed for 1.5 h under vacuum. Then, they were dried overnight at 393 K and the dried samples were 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 bimetallic Pt-Ni/ δ - Al_2O_3 catalyst was prepared through a sequential route in which the Pt precursor solution was impregnated over initially prepared and calcined Ni/ δ - Al_2O_3 catalyst. After Pt-Ni/ δ - Al_2O_3 slurry was dried, it was calcined at 773 K for 4 h. Particulate catalysts prepared are presented in Table 3.5.

As a result of the calcination, the catalyst is in oxide form and generally inactive for the reactions to be studied. In order to obtain high catalytic activity sites on catalyst surface, a pretreatment procedure involving the reduction of the metals from their oxide state to metallic state is required prior to reaction. Reduction procedure plays a crucial role in catalytic activity of metallic sites and should be developed for the reaction of interest. It can be defined by applying TPR (Temperature Programmed Reduction) on the catalyst under a reducing agent. Reviewing literature, a few alternative procedures were identified. One alternative to reduce the monometallic Ni catalyst is treatment at 873 K under hydrogen (Ma, 1995). The other alternative is reducing the catalysts at 773 K for 4 h under hydrogen. In addition, it is reported that Ni/ γ - Al_2O_3 catalyst can be reduced at 1123 K for half an hour under pure hydrogen flowing at 30 cm³·min⁻¹ (Mukainaken *et al.*, 2008). Considering these reports, a reduction procedure was proposed for the catalysts prepared in this work. The details of this procedure are shown in Figure 3.6. After placing the catalyst in the quartz reactor, N₂ was allowed to flow at 20 cm³·min⁻¹ and heated at a rate of 10

K/min, to the temperature steps of 523 K, 673 K and 973 K, respectively. The gas flow was switched from N₂ to pure H₂ (25 cm³·min⁻¹) to reduce catalysts for 2 h with H₂. Then, temperature was cooled to reaction the temperature.

Table 3.5. Particulate catalysts prepared.

#	Catalyst	Active Metal, %	Particle Size, mesh
1	Ni/ δ -Al ₂ O ₃	15	10-18
2	Ni/ δ -Al ₂ O ₃	15	18-20
3	Ni/ δ -Al ₂ O ₃	15	20-30
4	Ni/ δ -Al ₂ O ₃	15	30-45
5	Ni/ δ -Al ₂ O ₃	15	45-60
6	Pt-Ni/ δ -Al ₂ O ₃	0.2- 15	45-60
7	Pd/ δ -Al ₂ O ₃	2	45-60
8	Pd/ δ -Al ₂ O ₃	2	60-80
9	Rh/ δ -Al ₂ O ₃	2	?10
10	Rh/ δ -Al ₂ O ₃	2	10-18
11	Rh/ δ -Al ₂ O ₃	2	18-20
12	Rh/ δ -Al ₂ O ₃	2	20-30
13	Rh/ δ -Al ₂ O ₃	2	30-45
14	Rh/ δ -Al ₂ O ₃	2	45-60
15	Rh/ δ -Al ₂ O ₃	2	60-80
16	Ru/ δ -Al ₂ O ₃	2	45-60
17	Ru/ δ -Al ₂ O ₃	2	60-80

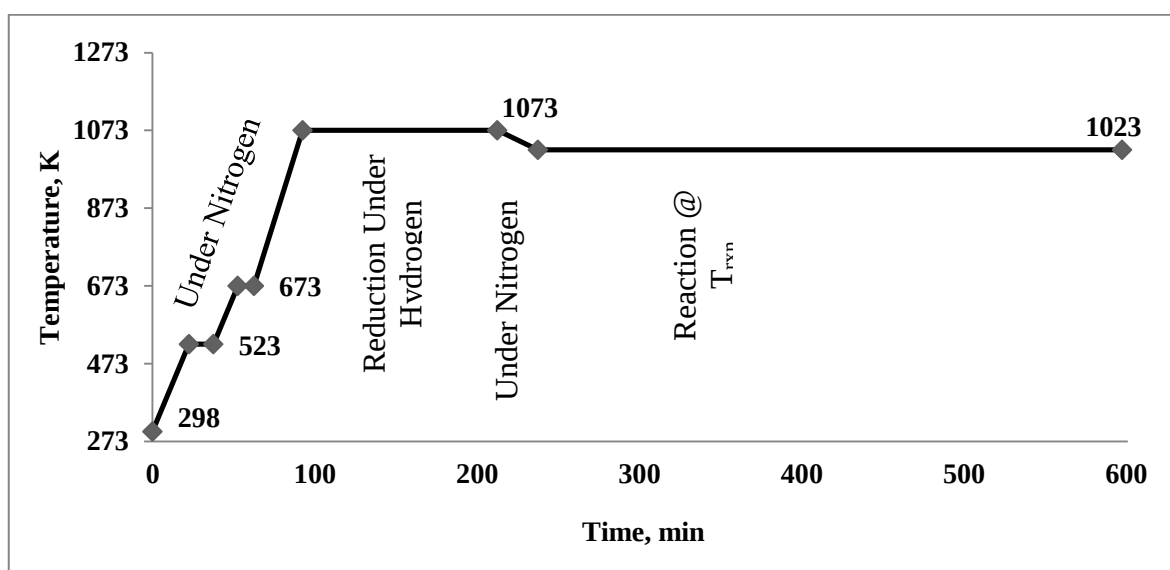


Figure 3.6. Proposed reduction procedure for Ni catalysts.

3.3.3. Coated Catalyst Preparation and Pretreatment

The same 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 $\gamma\text{-Al}_2\text{O}_3$ (Alfa Aesar) powder with 3 μm particle size is used for synthesizing the catalyst powders. After heat treatment to convert it to $\delta\text{-Al}_2\text{O}_3$, predetermined amount of catalyst powder is mixed with a definite amount of deionized water containing a calculated amount of the precursor concerned, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Rh}(\text{NO}_3)_3$, $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ or $\text{Ru}(\text{NO})(\text{NO}_3)_3$, 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 x 5 mm x 25 mm (height x width x 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 (Aartun *et al.*, 2004). 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. Catalyst coatings prepared are presented in Table 3.6.

Table 3.6. Coated catalysts prepared.

#	Catalyst	Active Metal, %	Particle Size, μm
1	Ni/ $\delta\text{-Al}_2\text{O}_3$	10	3
2	Pd/ $\delta\text{-Al}_2\text{O}_3$	2	3
3	Rh/ $\delta\text{-Al}_2\text{O}_3$	2	3
4	Ru/ $\delta\text{-Al}_2\text{O}_3$	2	3

3.4. Reaction Tests

3.4.1. Blank Tests

Blank tests were conducted to ensure that the material of construction, glass wool and the reactor did not interfere with the reaction test outputs. The results indicated that the glass wool and the reactor were inert under the conditions used in the reaction experiments. Catalyst supports ($\delta\text{-Al}_2\text{O}_3$) were also found inert under the conditions studied.

3.4.2. Preliminary Tests

Decreasing (Decreasing Temperature Progression, DTP) and increasing (Increasing Temperature Progression, ITP) reaction temperature programs were followed for selected parameters. Preliminary tests were performed for MSR to characterize the experimental setup. To prevent external and internal mass transfer resistances in the conventional packed-bed microreactor, the following criteria were tested. In this context, inert support $\delta\text{-Al}_2\text{O}_3$ was used as diluent to increase catalyst bed height and to evenly distribute the catalyst in the bed for meeting the following criteria. A series of experiments were performed at different diluent amounts of 525, 775 and 1125 mg at a constant catalyst amount of 225 mg using 15%Ni/ $\delta\text{-Al}_2\text{O}_3$. $L_{\text{cat-bed}}$ necessary for ensuring plug flow conditions in the packed-bed microreactor was determined as 19 mm. Internal diffusion

resistances and their effect on reaction rates and the H_2/CO ratio in product gases were tested at 873-1048 K using three different progressively decreasing particle sizes.

3.4.3. MSR in Conventional Packed Bed Reactor

Syngas production by methane steam reforming was investigated in packed-bed microreactors over various catalysts including $Ni/\delta-Al_2O_3$, $Pt-Ni/\delta-Al_2O_3$, $Pd/\delta-Al_2O_3$, $Rh/\delta-Al_2O_3$ and $Ru/\delta-Al_2O_3$. The quality of syngas, i.e., molar H_2/CO ratio in the product stream and methane conversion were investigated in terms of reaction temperature, molar steam-to-carbon (S/C) ratio, particle size and addition of carbondioxide to the feed over these catalysts. The results were compared for selecting the catalyst composition(s) that are most suitable for coating onto micro-channel surfaces or packing into micro-channels in a later phase of the project. The details of the experiments that were conducted on $Ni/\delta-Al_2O_3$, $Pt-Ni/\delta-Al_2O_3$, $Pd/\delta-Al_2O_3$, $Rh/\delta-Al_2O_3$ and $Ru/\delta-Al_2O_3$ catalysts are given in Tables 3.7- 3.11.

Table 3.7. MSR experiments on 15%Ni/ δ -Al₂O₃ reduced at 1023 K for 2 h.

#	Catalyst	Temp., K	W _{cat} , mg	S/C	CH ₄ , cm ³ · min ⁻¹	CO ₂ , cm ³ · min ⁻¹	Flow rate, cm ³ ·min ⁻¹	Particle Size, mesh
1	15%Ni/ δ -Al ₂ O ₃	973	150	2.5	8	0.0	80	45-60
2	15%Ni/ δ -Al ₂ O ₃	973	150	2.5	10	0.0	100	45-60
3	15%Ni/ δ -Al ₂ O ₃	973	180	2.5	12	0.0	120	45-60
4	15%Ni/ δ -Al ₂ O ₃	973	225	2.5	15	0.0	150	45-60
5	15%Ni/ δ -Al ₂ O ₃	973	270	2.5	18	0.0	180	45-60
6	15%Ni/ δ -Al ₂ O ₃	973	300	2.5	20	0.0	200	45-60
7	15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	45-60
8	15%Ni/ δ -Al ₂ O ₃	923	225	2.5	15	0.0	150	45-60
9	15%Ni/ δ -Al ₂ O ₃	873	225	2.5	15	0.0	150	45-60
10	15%Ni/ δ -Al ₂ O ₃	973	225	3.0	15	0.0	150	45-60
11	15%Ni/ δ -Al ₂ O ₃	973	225	3.5	15	0.0	150	45-60
12	15%Ni/ δ -Al ₂ O ₃	973	225	2.0	15	0.0	150	45-60
13	15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	30-45
14	15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	20-30
15	15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	18-20
16	15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	15	150	45-60
17	15%Ni/ δ -Al ₂ O ₃	973	225	2.5	15	15	150	45-60
18	15%Ni/ δ -Al ₂ O ₃	923	225	2.5	15	15	150	45-60
20	15%Ni/ δ -Al ₂ O ₃	873	225	2.5	15	15	150	45-60

Table 3.8. MSR experiments on 0.2%Pt-15%Ni/ δ -Al₂O₃ reduced at 1073 K for 2 h.

#	Catalyst	Temp., K	W _{cat} , mg	S/C	CH ₄ , cm ³ · min ⁻¹	CO ₂ , cm ³ · min ⁻¹	Flow rate, cm ³ ·min ⁻¹	Particle Size, mesh
1	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	45-60
2	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	973	225	2.5	15	0.0	150	45-60
3	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	923	225	2.5	15	0.0	150	45-60
4	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	873	225	2.5	15	0.0	150	45-60
5	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	1023	225	2.5	15	15	150	45-60
6	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	973	225	2.5	15	15	150	45-60
7	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	923	225	2.5	15	15	150	45-60
8	0.2%Pt- 15%Ni/ δ -Al ₂ O ₃	873	225	2.5	15	15	150	45-60

Table 3.9. MSR experiments on 2%Pd/ δ -Al₂O₃ reduced at 1073 K for 2 h.

#	Catalyst	Temp., K	W _{cat} , mg	S/C	CH ₄ , cm ³ . min ⁻¹	CO ₂ , cm ³ . min ⁻¹	Flow rate, cm ³ . min ⁻¹	Particle Size, mesh
1	2%Pd/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	45-60
2	2%Pd/ δ -Al ₂ O ₃	973	225	2.5	15	0.0	150	45-60
3	2%Pd/ δ -Al ₂ O ₃	923	225	2.5	15	0.0	150	45-60
4	2%Pd/ δ -Al ₂ O ₃	873	225	2.5	15	0.0	150	45-60
5	2%Pd/ δ -Al ₂ O ₃	1023	225	2.5	15	15	150	45-60
6	2%Pd/ δ -Al ₂ O ₃	973	225	2.5	15	15	150	45-60
7	2%Pd/ δ -Al ₂ O ₃	923	225	2.5	15	15	150	45-60
8	2%Pd/ δ -Al ₂ O ₃	873	225	2.5	15	15	150	45-60

Table 3.10. MSR experiments on 2%Ru/ δ -Al₂O₃ reduced at 1073 K for 2 h.

#	Catalyst	Temp., K	W _{cat} , mg	S/C	CH ₄ , cm ³ . min ⁻¹	CO ₂ , cm ³ . min ⁻¹	Flow rate, cm ³ .min ⁻¹	Particle Size, mesh
1	2%Ru/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	45-60
2	2%Ru/ δ -Al ₂ O ₃	973	225	2.5	15	0.0	150	45-60
3	2%Ru/ δ -Al ₂ O ₃	923	225	2.5	15	0.0	150	45-60
4	2%Ru/ δ -Al ₂ O ₃	873	225	2.5	15	0.0	150	45-60
5	2%Ru/ δ -Al ₂ O ₃	1023	225	2.5	15	15	150	45-60
6	2%Ru/ δ -Al ₂ O ₃	973	225	2.5	15	15	150	45-60
7	2%Ru/ δ -Al ₂ O ₃	923	225	2.5	15	15	150	45-60
8	2%Ru/ δ -Al ₂ O ₃	873	225	2.5	15	15	150	45-60

Table 3.11. MSR experiments on 2%Rh/ δ -Al₂O₃ catalyst reduced at 1073 K for 2 h.

#	Catalyst	Temp., K	W _{cat} , mg	S/C	CH ₄ , cm ³ · min ⁻¹	CO ₂ , cm ³ · min ⁻¹	Flow rate, cm ³ · min ⁻¹	Particle Size, mesh
1	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	45-60
2	2%Rh/ δ -Al ₂ O ₃	973	225	2.5	15	0.0	150	45-60
3	2%Rh/ δ -Al ₂ O ₃	923	225	2.5	15	0.0	150	45-60
4	2%Rh/ δ -Al ₂ O ₃	873	225	2.5	15	0.0	150	45-60
5	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	<10
6	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	10-18
7	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	20-30
8	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	0.0	150	30-45
9	2%Rh/ δ -Al ₂ O ₃	1023	225	2.5	15	15	150	45-60
10	2%Rh/ δ -Al ₂ O ₃	973	225	2.5	15	15	150	45-60
11	2%Rh/ δ -Al ₂ O ₃	923	225	2.5	15	15	150	45-60
12	2%Rh/ δ -Al ₂ O ₃	873	225	2.5	15	15	150	45-60

3.4.4. MSR in Packed and Coated Microchannel Reactors (MCR)

The major aim of this part of the study is 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. Methane steam reforming experiments were carried out within a wide test matrix and involved testing of δ -Al₂O₃ supported 2% (by weight) Rh, 2% Ru and 2% Pd catalysts together with the conventional 10% Ni catalyst 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 carbon (or methane, since there is one mole of carbon per mole of methane) at the inlet.

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 x 30 mm (outer diameter x length) (Figure 3.7). The interior of the housing is shaped with the wire electro discharge machining technique, such that the coated plate can be 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 x 4 mm x 25 mm (height x width x 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 . 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 (Figure 4.22) as measured by the cross-sectional ESEM images of the coated plates. 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 (Figure 3.7).

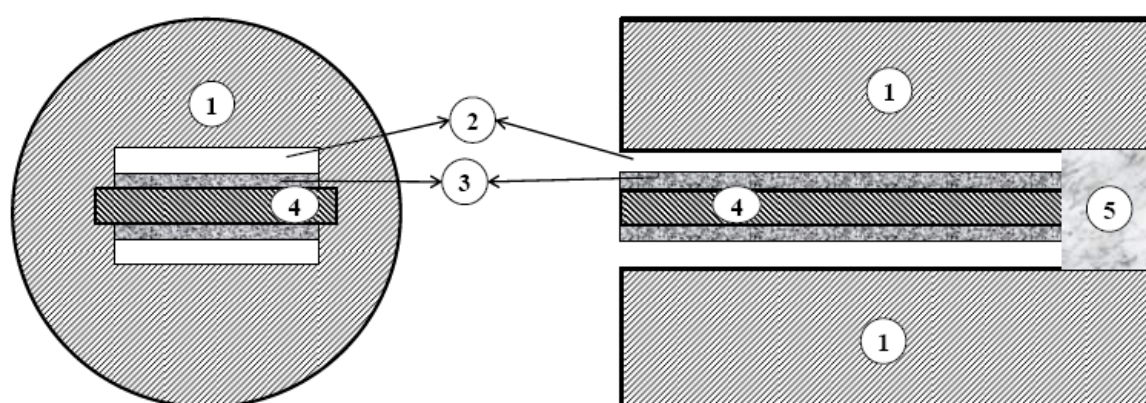


Figure 3.7. Top (at the left) and cross-sectional (at the right) views of the coated microchannel configuration (1: Engineered metal housing; 2: Open microchannels; 3: Coated catalyst layers; 4: FeCrAlY plate; 5: Ceramic wool plug).

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 Figure 3.7. The resulting gaps form two microchannels, each having dimensions of 0.75 mm x 4 mm x 25 mm (height x width x 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.

Before the reaction tests, the catalysts are reduced in situ by $25 \text{ cm}^3 \text{ min}^{-1}$ of pure hydrogen flow at 1073 K for 2 h. During the experiments, total flow rates and catalyst weights in both reactor configurations are kept constant at $90 \text{ cm}^3 \cdot \text{min}^{-1}$ and 0.065 g, respectively. In testing the effect of temperature, feed composition is fixed at a volumetric $\text{CH}_4:\text{H}_2\text{O}:\text{N}_2$ ratio of 10:25:65, while the studies on the effect of the S/C ratio are conducted by changing the steam and nitrogen flow rates so as to keep the methane and total flow rates constant at 9 and $90 \text{ cm}^3 \cdot \text{min}^{-1}$, 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 ($W_{\text{cat}}/F_{\text{CH}_4,0}$) equal to $7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ (which corresponds to ca. 75 ms based on total microchannel volume including the catalyst). This definition of contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$) is preferred since it is independent of whether the catalyst is in the form of particles or is wall-coated (Kolb, 2008). 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 to 9 hours.

3.4.5. OSRM in Packed Microchannel Reactors (MCR)

The aim of this part of the study was to assess and compare the oxidative steam reforming of methane (OSRM) performances of two typical microchannel reactor configurations – wall-coated and packed – that are operated under identical conditions in a wide range of parameter values including residence time, reaction temperature, inlet steam-to-carbon (S/C) and (O_2/C) molar ratios. Experiments were carried out within a wide test matrix and involved testing of alumina supported 2%Rh-0.2%Pt (by weight) catalyst at different temperatures, molar steam-to-carbon ratios and oxygen-to-carbon ratios as well as residence time through a parametric approach. The experiments in packed microchannel reactors were conducted in this study while those involving coated microchannel reactors were performed by Karakaya (2012). Additionally, the oxidative steam reforming of methane (OSRM) performance of monometallic 2%Rh/ $\delta\text{-Al}_2\text{O}_3$ catalyst was investigated

with in a wide range of parameter values including residence time, reaction temperature, inlet steam-to-carbon (S/C) and (O_2/C) molar ratios.

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 x 30 mm (outer diameter x length) (Figure 3.8). The interior of the housing is shaped with the wire electro discharge machining technique, such that two plates can be inserted face-to face to create in between a single microchannel having dimensions of 0.75 mm x 4 mm x 20 mm (height x width x depth). The two reactor configurations studied involve (a) two uncoated plates with catalyst packing in the single microchannel volume in between and (b) two plates coated with catalyst only on the side facing each other to give a two walls-coated single catalytic microchannel,. The former configuration was studied in this work using a catalyst mass equal to the total coated catalyst mass in the latter configuration, which was tested by Karakaya (2012). After insertion, the catalyst layers at both walls of the microchannel 0.5 mm zones of the plate are scraped to overlap between the plates and grooves and to give a total remaining coating mass of 0.0107 g (Figure 3.13). 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 (Simsek *et al.*, 2011) as measured by the cross-sectional ESEM images of the coated plates. 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 (Figure 3.8)

OSRM experiments were carried out at 773, 823, 873 and 923 K and at atmospheric pressure with steam-to-carbon-ratios of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, and oxygen-to-carbon ratios of 0.0, 0.47, 0.54 and 0.63, at weight-based contact times of 0.35, 0.41, 0.50 and 0.71 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$. Steam-to-carbon (S/C) ratio and oxygen-to-carbon (O_2/C) ratio are defined as the ratio of the number of moles of steam and oxygen to that of carbon (or methane) at the inlet, respectively. Before the reaction tests, the catalysts are reduced in situ under $25\text{ cm}^3\cdot\text{min}^{-1}$ 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. High purity dry air is used for the oxygen supply. Flow rates of methane, dry air and diluents 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 all the experiments, total flow rates and catalyst weights in both reactor configurations are kept constant at $210 \text{ cm}^3 \cdot \text{min}^{-1}$ and 0.0107 g, respectively, except in residence time experiments. In testing the effect of temperature on OSRM performance of the bimetallic Pt-Rh catalyst, feed composition was fixed at a volumetric $\text{CH}_4:\text{H}_2\text{O}:\text{Air}:\text{N}_2$ ratio of 14.28:42.85:32.08:10.77, while studies on the effect of the molar S/C and O_2/C ratios were conducted by changing the steam, air and nitrogen flow rates so as to keep the methane and total flow rates constant at 30 and $210 \text{ cm}^3 \cdot \text{min}^{-1}$, respectively. The same plan of experiments was applied to both packed and coated microchannel configurations, which are compared on the basis of identical contact time defined as the ratio of catalyst weight to inlet methane flow rate ($W_{\text{cat}}/F_{\text{CH}_4,0}$) equal to $0.35 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ (which corresponds to ca. 3.63 ms based on total microchannel volume including the catalyst). This definition of contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$) is preferred since it is independent of whether the catalyst is in the form of particles or is wall-coated (Kolb, 2008). All results reported in this study are based on product data collected 90 min after the start-up of the OSR reaction.

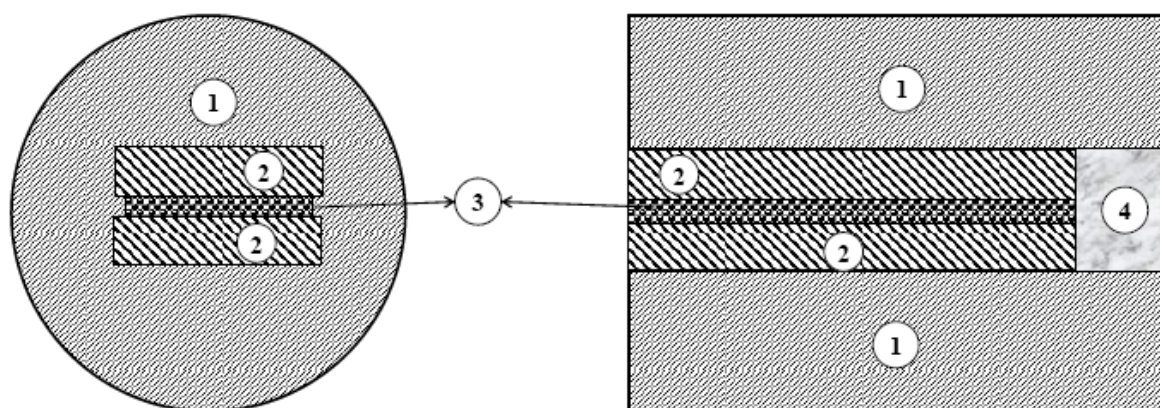


Figure 3.8. Top (at the left) and cross-sectional (at the right) views of the coated microchannel configuration (1: Engineered metal housing; 2: FeCrAlY plate; 3: Single microchannel packed with catalyst or coated with catalyst layers on each face; 4: Ceramic wool plug).

Reactant and product analysis was conducted using a Shimadzu GC-14B gas chromatograph that is equipped with a Carboxen 1000 packed column and a thermal

conductivity detector held at 448 K. To separate the gases, the column temperature was programmed to hold at 323 for 13 min, then to ramp to 450 K in 2 min hold there for another 8.5 min. The products, H₂, N₂, CH₄, CO and CO₂ were all detected in the same column under argon carrier gas flow of 25 cm³·min⁻¹. Since the Carboxen 1000 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.

4. RESULTS AND DISCUSSION

The results of this study are presented and discussed in three sections:

- Characterization and MSR in conventional packed bed microreactor over various δ - Al_2O_3 supported catalysts including Ni, Pt-Ni, Pd, Rh and Ru.
- Characterization and comparison of the MSR performances of δ - Al_2O_3 supported 2% Rh, 2% Ru and 2% Pd (by weight) catalysts together with 10% Ni (by weight) catalyst for syngas production in two different microchannel reactor geometries, namely wall-coated and packed microchannels.
- Characterization and comparison of the performances of δ - Al_2O_3 supported 2% Rh-0.2% Pt bimetallic catalyst for OSRM over packed and coated microchannel reactor configurations, as well as comparison of the performances of δ - Al_2O_3 supported 2%Rh-0.2%Pt bimetallic and monometallic 2%Rh particulate catalysts in the packed single microchannel configuration.

Methane conversion (X_{CH_4}) is calculated by means of a carbon balance between the reactant CH_4 and the gaseous products CO and CO_2 , and also by the percent difference between inlet and outlet CH_4 :

$$X_{\text{CH}_4} = 100 \times \frac{y_{\text{CO}} + y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{CH}_4}} \quad (4.1)$$

$$X_{\text{CH}_4} = 100 \times \frac{F_{\text{CH}_4}^{\text{in}} + F_{\text{CH}_4}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}}} \quad (4.2)$$

Proximity of the results obtained from Equations 1 and 2 implies coke-free operation since all the methane will have been converted to the detectable gaseous products. The other important experimental result, CO selectivity (S_{CO}), is defined as

$$S_{\text{CO}} = 100 \times \frac{y_{\text{CO}}}{y_{\text{CO}} + y_{\text{CO}_2}} \quad (4.3)$$

In Equations 4.1 and 4.3, y_i (i: CO, CO₂, CH₄) denotes the species mole fractions on a dry basis, and $F_{\text{CH}_4}^{\text{in}}$ and $F_{\text{CH}_4}^{\text{out}}$ denote the number of moles of methane at the reactor inlet and outlet, respectively.

4.1. MSR in Conventional Packed Bed Microreactor

The first part of this experimental study involves the screening of several alumina supported monometallic and bimetallic catalysts for methane steam reforming (MSR). The major aim of catalyst screening is to obtain consistent data on activity, selectivity and stability for a range of solid catalyst samples in order to select the best candidate(s) for the reaction to be studied. The reaction data obtained for this purpose must accurately reflect steady-state chemical activity and selectivity of each catalyst sample. Catalyst evaluation, kinetic modeling and reactor assessment must depend on data that reflect only the chemical events, which means that, initially, physical transport phenomena arising from fluid flow pattern, catalyst physical properties or reactor geometry must nearly be eliminated at both reactor and particle scales (Önsan, 2010).

Fixed-bed reactors packed with solid particles are commonly chosen for screening solid catalysts. The simplest case is a two-phase fixed-bed microreactor in which the solid catalyst is contacted with reactants in the gas phase. Since fluid flow pattern defines the performance of continuous reactors, attention must be paid to ensure ideal plug-flow at the reactor scale. Furthermore, isothermal operation and elimination of external and internal heat and mass transport effects at the particle scale are equally important to evaluate the actual chemical activity and selectivity of solid catalysts.

Therefore, in the first part of the present work, preliminary parametric studies were conducted in conventional packed bed microreactors in order to determine the conditions under which all transport effects are eliminated at both reactor and particle scales, and to observe only the chemical events that prevail. The catalyst performance test conditions were then designed within these conditions to investigate the effects of the reaction temperature, molar steam-to-carbon (S/C) ratio, and addition of carbondioxide to the feed over various catalysts including Ni/ δ -Al₂O₃, Pt-Ni/ δ -Al₂O₃, Pd/ δ -Al₂O₃, Rh/ δ -Al₂O₃ and Ru/ δ -Al₂O₃ on MSR activity for methane conversion and H₂/CO ratio in the product

stream. The catalysts tested were characterized by ESEM-EDX and XRD to determine their physical and chemical properties. Conventional microreactor studies provided the basis for selecting the catalysts for further work on packed and coated microchannel reactors.

4.1.1. Catalyst Characterization

The detailed characterization of 0.2%Pt-15%Ni/ δ -Al₂O₃ catalyst was reported (Selen, 2003; Caglayan *et al.* 2005) earlier, pointing out the changes on the catalyst surface and active metallic sites due to reduction. From the analytical mapping of the SEM image of this catalyst in Figure 4.1, it is clearly seen that (i) 15 % Ni almost covers the support surface, and (ii) Pt sites are dispersed homogeneously forming Pt sites in the close neighborhood of Ni sites. In addition, there is no indication of Pt–Ni alloy formation either locally or in the bulk as confirmed by EDS and XRD (Figures 4.1 and 4.2), respectively.

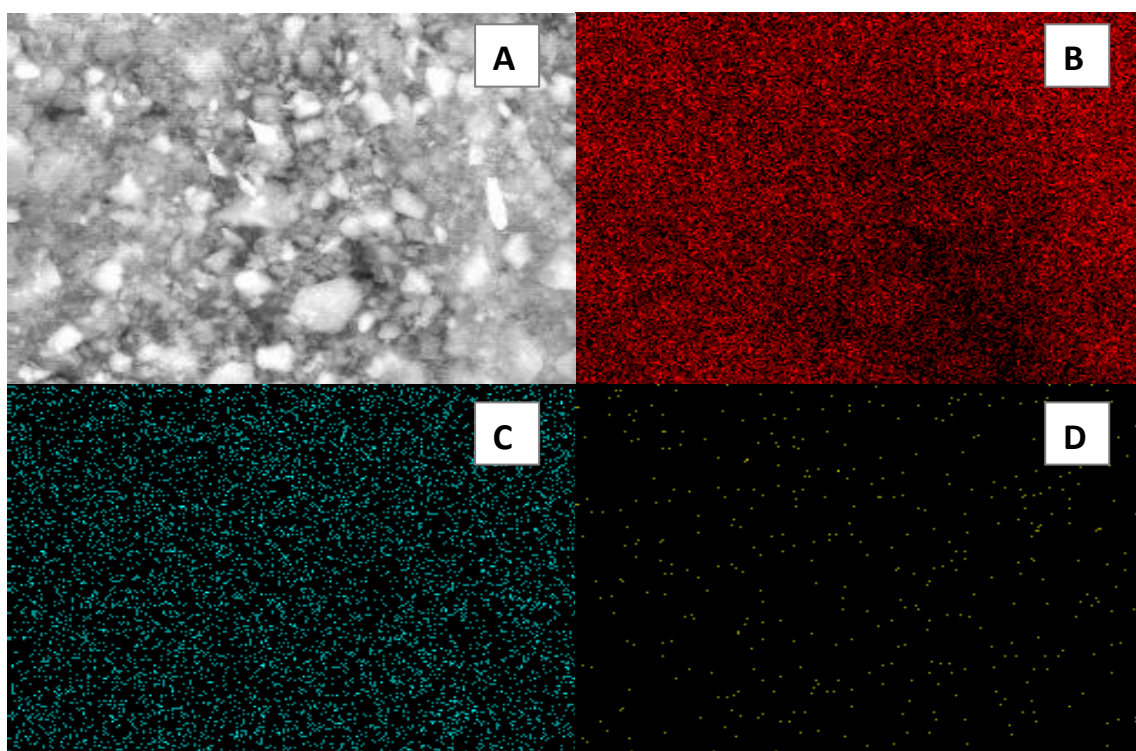


Figure 4.1. SEM and analytical mapping images of 0.2%Pt-15%Ni/ δ -Al₂O₃ (A: SEM image, B: Al₂O₃, C: Ni, D: Pt. (Magn: 100000 $\times$).

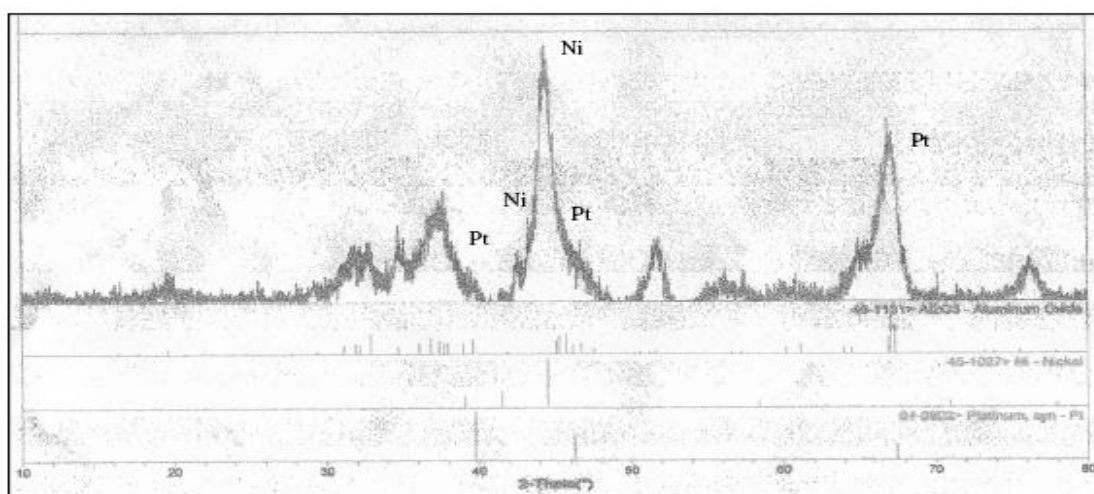


Figure 4.2. XRD pattern of the reduced 0.2wt%Pt-15wt%Ni/ δ -Al₂O₃ catalyst (Lillo-Rodenas *et al.*, 2003).

The SEM images of the monometallic 15%Ni/ δ -Al₂O₃ catalyst are shown in Figure 4.3. It can be said that the Ni sites (i) mostly cover the δ -Al₂O₃ surface, and (ii) are dispersed homogenously. EDX analysis shows that the impregnated Ni content on the catalyst is 14.84% in parallel with the targeted amount of 15%.

The SEM images of the 2%Pd/ δ -Al₂O₃, 2%Rh/ δ -Al₂O₃ and 2%Ru/ δ -Al₂O₃ catalysts are presented in Figures 4.4 to 4.6 respectively. These images and mappings indicate homogeneous dispersion of the metals on the δ -Al₂O₃ support surface.

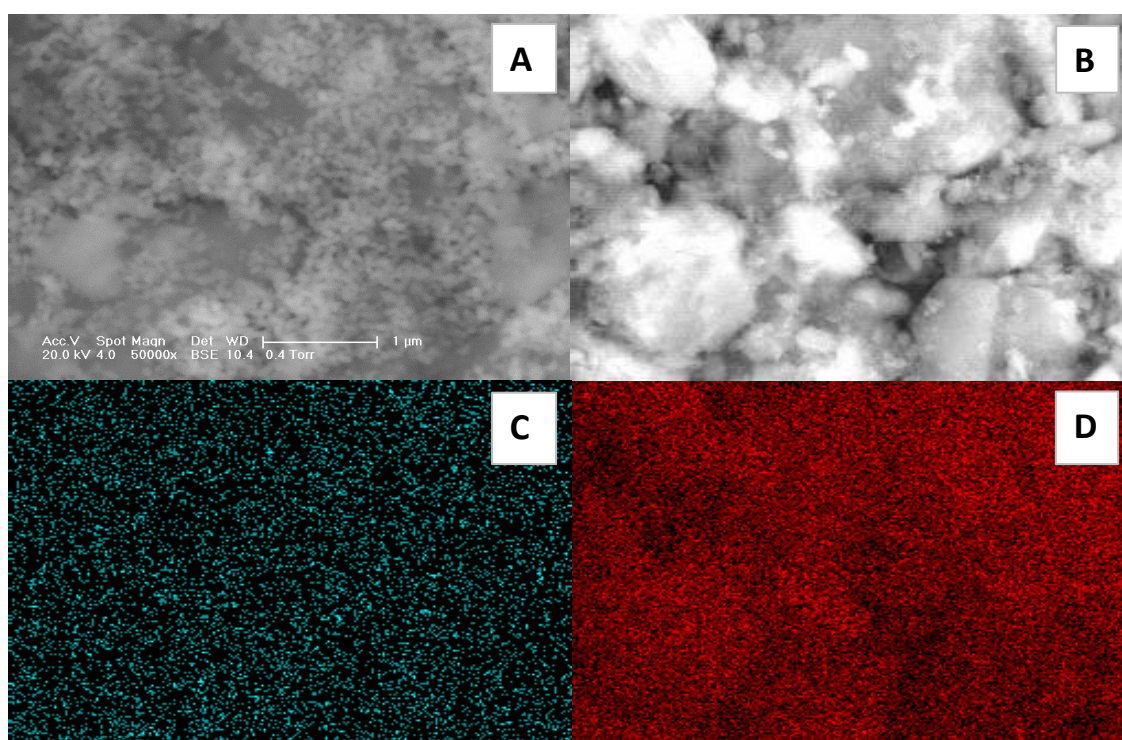


Figure 4.3. SEM and analytical mapping images of 15%Ni/ δ -Al₂O₃ (A: SEM image (50000 $\times$), B: SEM image for mapped area, C: Ni, D: Al₂O₃ (Magn: 10000 $\times$).

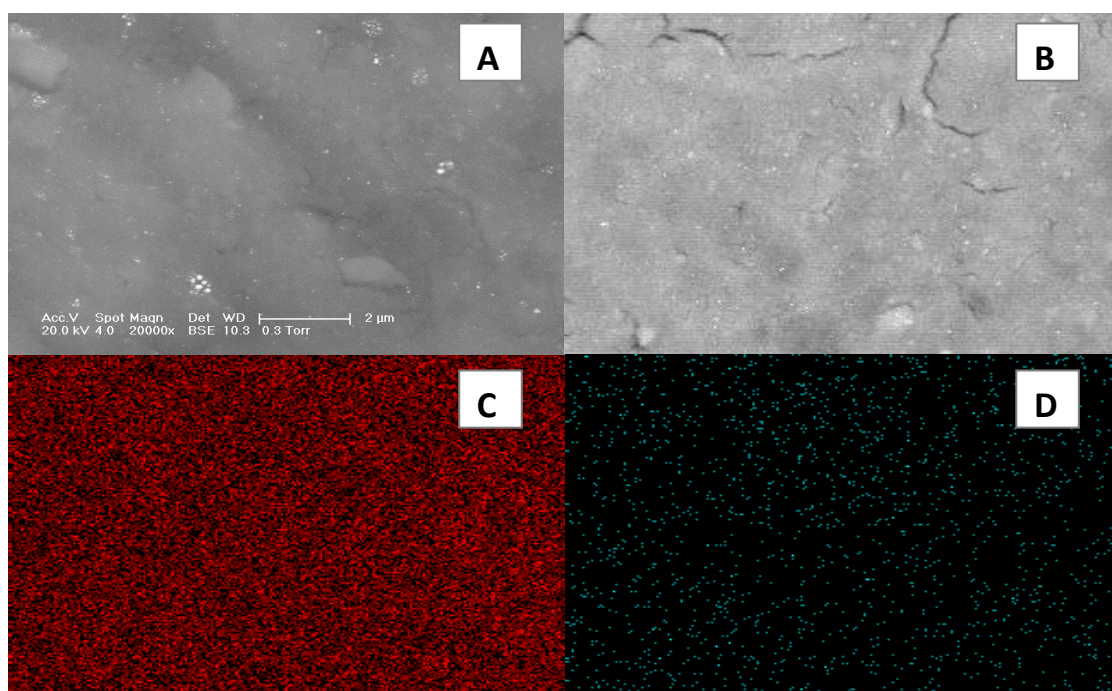


Figure 4.4. SEM and analytical mapping images of 2%Pd/ δ -Al₂O₃ (A: SEM image (20000 $\times$), B: SEM image for mapped area, C: Al₂O₃, D: Pd (Magn: 5000 $\times$).

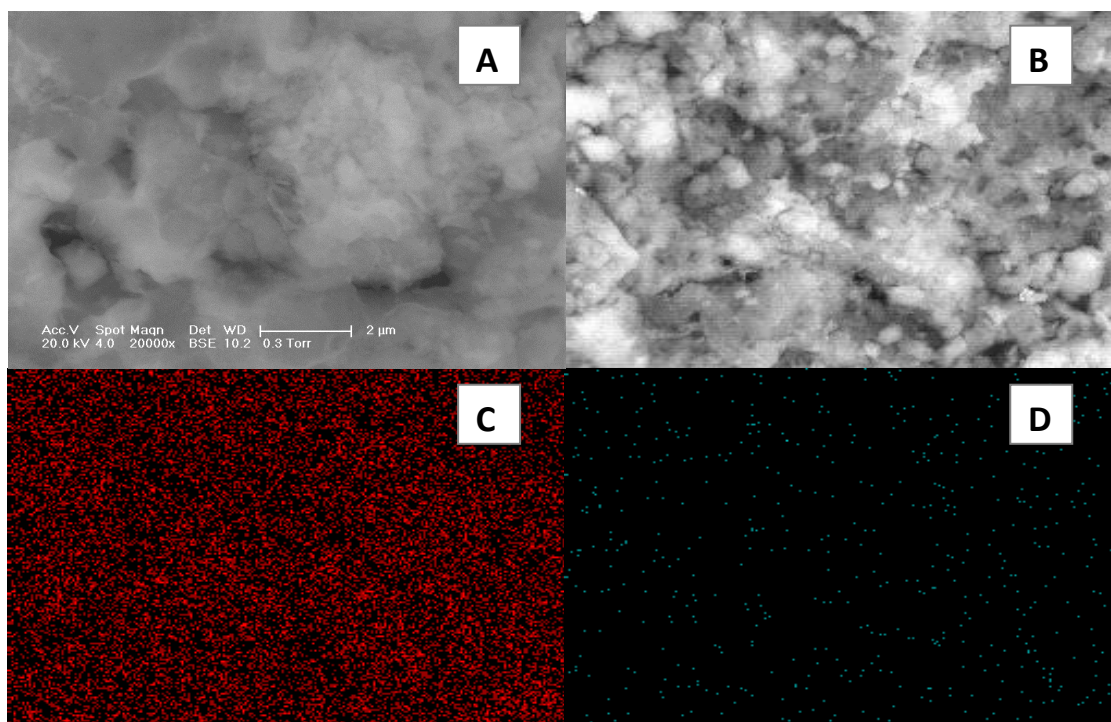


Figure 4.5. SEM and analytical mapping images of 2%Rh/ δ -Al₂O₃ (A: SEM image (20000 $\times$), B: SEM image for mapped area, C: Al₂O₃, D: Rh (Magn: 5000 $\times$).

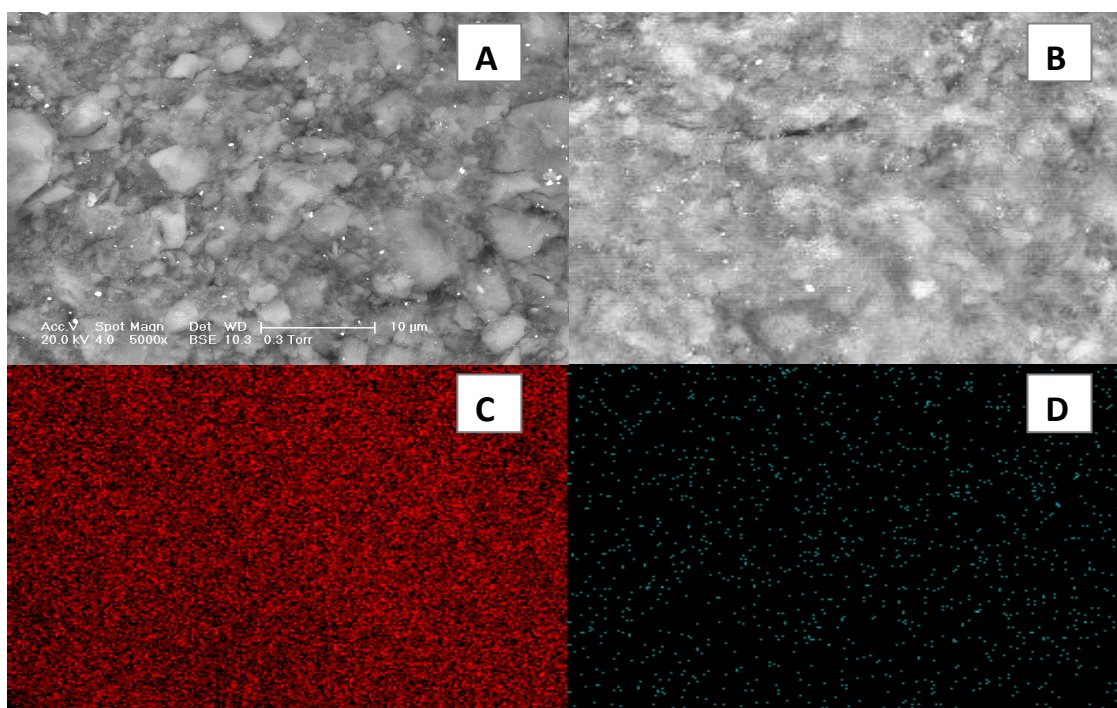


Figure 4.6. SEM and analytical mapping images of 2%Ru/ δ -Al₂O₃ (A: SEM image (5000 $\times$), B: SEM image for mapped area, C: Al₂O₃, D: Rh (Magn: 5000 $\times$).

4.1.2. Fluid Flow Pattern at the Reactor Scale

In packed-bed reactors, the void fraction in the wall region is higher than in the central part of the bed; therefore, in order to eliminate the wall effect on the flow pattern, a rule of thumb is to select a reactor tube diameter to particle diameter ratio greater than 15.

$$D_{\text{tube}} / D_{\text{particle}} > 15$$

Axial gradients may exist in the reactor as a result of reactant conversion which distorts the plug flow profile, and in order to minimize axial dispersion, a rule of thumb for first order reactions is to keep the ratio of packed reactor length to particle diameter greater than 50, in the range of particle Reynolds numbers close to 10 or Peclet numbers around 2.

$$L_{\text{tube}} / D_{\text{particle}} > 50$$

Packed-bed laboratory microreactors make use of very small particle diameters, leading to lower particle Reynolds numbers, which means that the $L_{\text{tube}} / d_{\text{particle}}$ ratio must certainly be as much higher than 50 as possible within experimental limits (Carberry, 1964).

Preliminary tests were performed for characterizing packed bed microreactor performance for MSR over 15%Ni/ δ -Al₂O₃ under conditions where transport effects are eliminated at macro and micro levels. The CH₄ conversions and H₂/CO ratios obtained by keeping the catalyst weight-based contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$) constant and using different packed bed lengths over 15%Ni/ δ -Al₂O₃ at 1023 K are plotted in Figure 4.7. The catalyst bed was diluted with inert support δ -Al₂O₃ to obtain different bed lengths. Figure 4.7 indicates that methane conversion remains constant after 19 mm bed length, which means that axial dispersion effects disappear. Similarly, H₂/CO reaches a constant level at the same bed length. The catalyst particle size used is 45-60 mesh, i.e. 250-350 μm , which can be taken as 0.3 mm on the average.

- Criteria minimizing axial dispersion; $L_{\text{cat-bed}}/D_{\text{particle}} > 50$, $19/0.30 = 63.3$
- Ensuring a flat velocity profile; $D_{\text{tube}}/D_{\text{particle}} = 10/0.30 \geq 33$

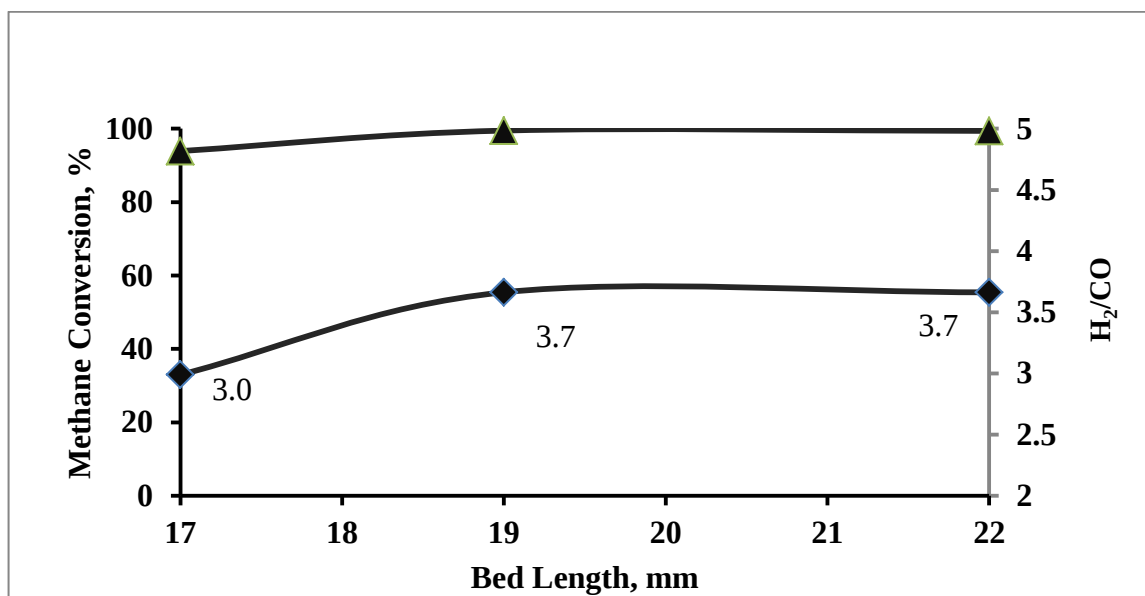


Figure 4.7. Effect of catalyst bed length on CH₄ conversion and H₂/CO ratio at 1023 K and S/C: 2.5 over 15%Ni/ δ -Al₂O₃ reduced at 1073 K for 2h (F_{total} =150 cm³min⁻¹).

4.1.3. Elimination of Internal Mass Transfer Effects at the Reactor Scale

In order to define the particle size range which eliminates internal diffusion resistances and their effect on the methane conversion and H₂/CO ratio in product gases, the MSR activity of the 15%Ni/ δ -Al₂O₃ catalyst was tested at four different average particle sizes in the range from 300 to 1500 μm at 1023 K with S/C:2.5, using fixed feed composition and constant contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$). The effect of average particle size is presented in Figure 4.8, which shows that methane conversion decreases from approximately 99% to 92% with increasing particle size, as a result of the role of internal transport resistances. On the other hand, H₂/CO increases from 2.3 to 3.2. Particle size experiments were also performed over 2%Rh/ δ -Al₂O₃ under similar conditions at four different average particle sizes ranging from 300 to 3000 μm (Figure 4.9). It is seen that methane conversion starts declining after 700 μm particle size due to internal transport resistances. Since it was also shown previously in our laboratories that a particle size range of 250-350 μm (45-60 mesh) eliminates internal diffusion effects (Akin, 1996), all subsequent experiments over the catalysts tested in the packed microreactor were conducted with this particle size range.

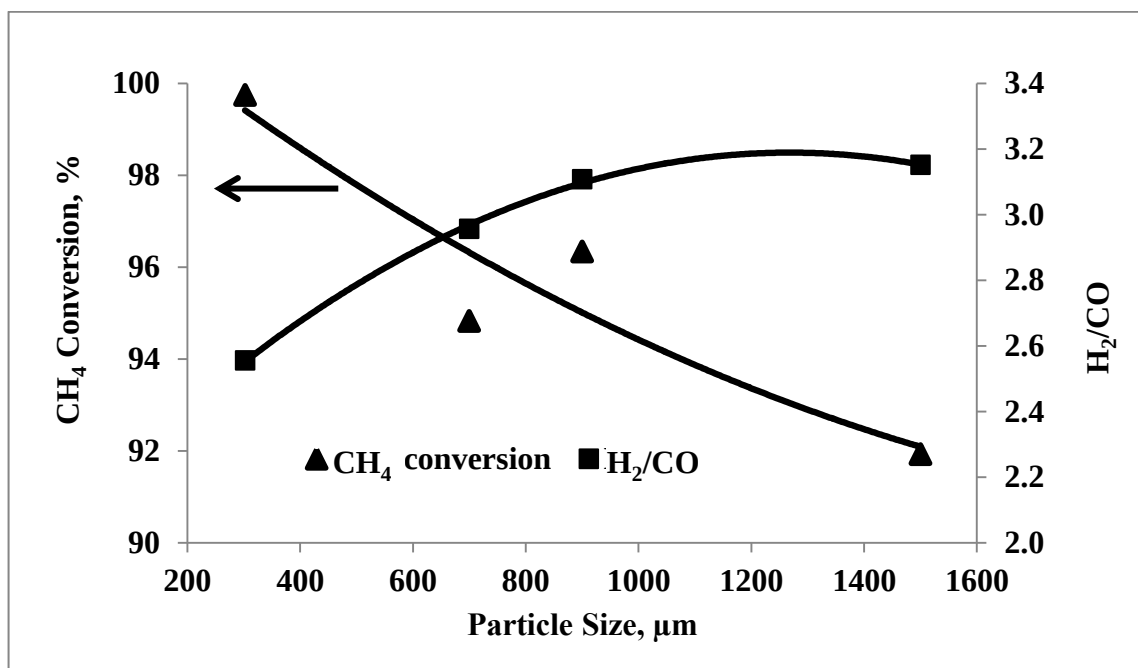


Figure 4.8. Methane conversion and H₂/CO over 15%Ni/δ-Al₂O₃ catalysts, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, at 1023 K, with S/C = 2.5.

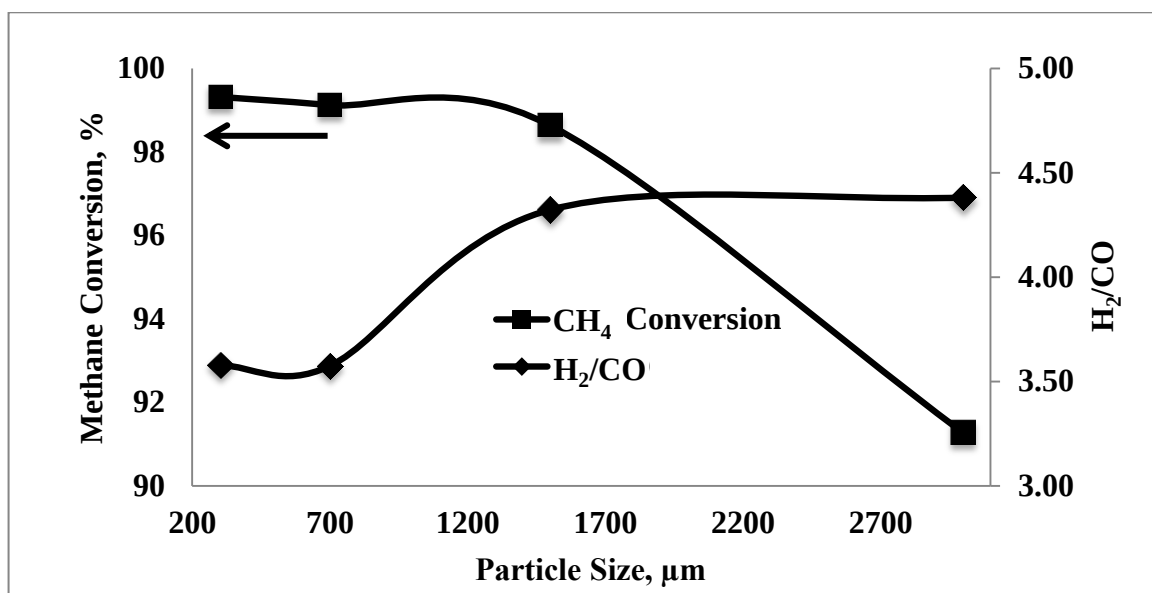


Figure 4.9. Methane conversion and H₂/CO over 2%Rh/δ-Al₂O₃ catalysts, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, at 1023 K, with S/C = 2.5.

4.1.4. Elimination of External Mass Transfer Effects at the Reactor Scale

In order to eliminate external transport resistances, the effect of flow rate was investigated over 15%Ni/ δ -Al₂O₃ at constant contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$) using various flow rates between 100-200 cm³·min⁻¹. The amount of catalyst in the packed bed microreactor was also changed so as to keep the contact time constant. The results are presented in Figure 4.10 as a function of linear velocity (m·s⁻¹) through the catalyst bed. External mass transfer effects were found to be negligible after 120 cm³·min⁻¹, and therefore, all other parametric studies were conducted using a total feed flow rate equal to or above 150 cm³·min⁻¹.

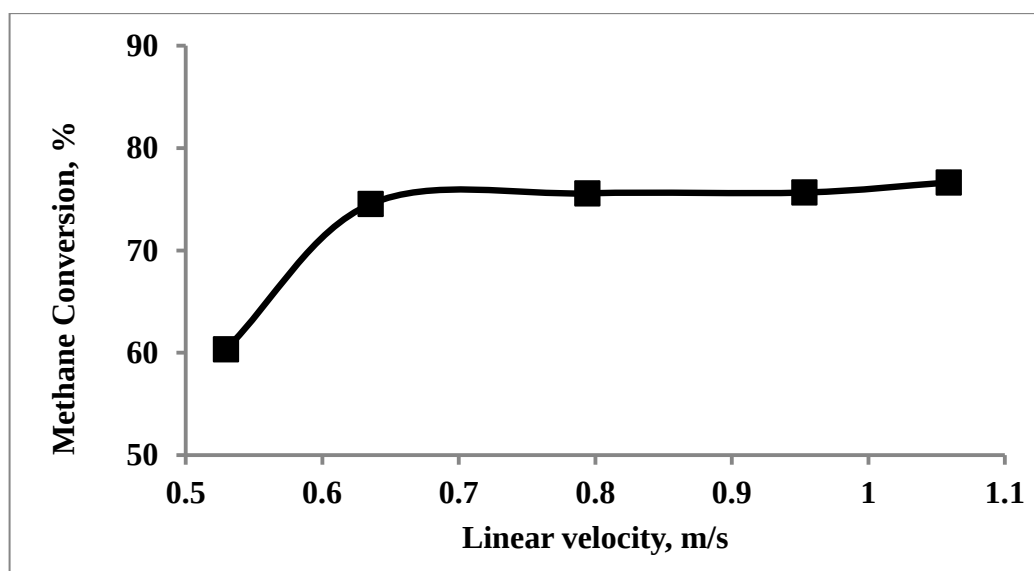


Figure 4.10. Effect of total flow rate on MSR over 15%Ni/ δ -Al₂O₃ reduced at 1073 K for 2h (reaction at 973 K, with S/C= 2.5 and ($W_{\text{cat}}/F_{\text{CH}_4,0}$ = 15).

4.1.5. Effect of Reaction Temperature

Effect of temperature on methane conversion and product H₂/CO ratio was investigated over various catalysts including Ni/ δ -Al₂O₃, Pt-Ni/ δ -Al₂O₃, Pd/ δ -Al₂O₃, Rh/ δ -Al₂O₃ and Ru/ δ -Al₂O₃ for determining their MSR activity, at 873, 923, 973 and 1023 K. The composition of the feed was fixed at CH₄/H₂O/N₂:10/25/65 by volume in testing the effects of temperature (Figure 4.11). Over all catalysts, methane conversion rises with -

temperature. The Rh-based catalyst was distinguished from others in that it was quite impervious to temperature changes, and exhibited relatively higher conversions even at lower temperatures. On the other hand, Pd based catalyst was the most susceptible one to temperature increase with conversions increasing from ca. 50% at 873 K to ca. 90% at 1023 K. It is found that at the highest temperature, all catalysts exhibit similar conversions close to equilibrium conversion level.

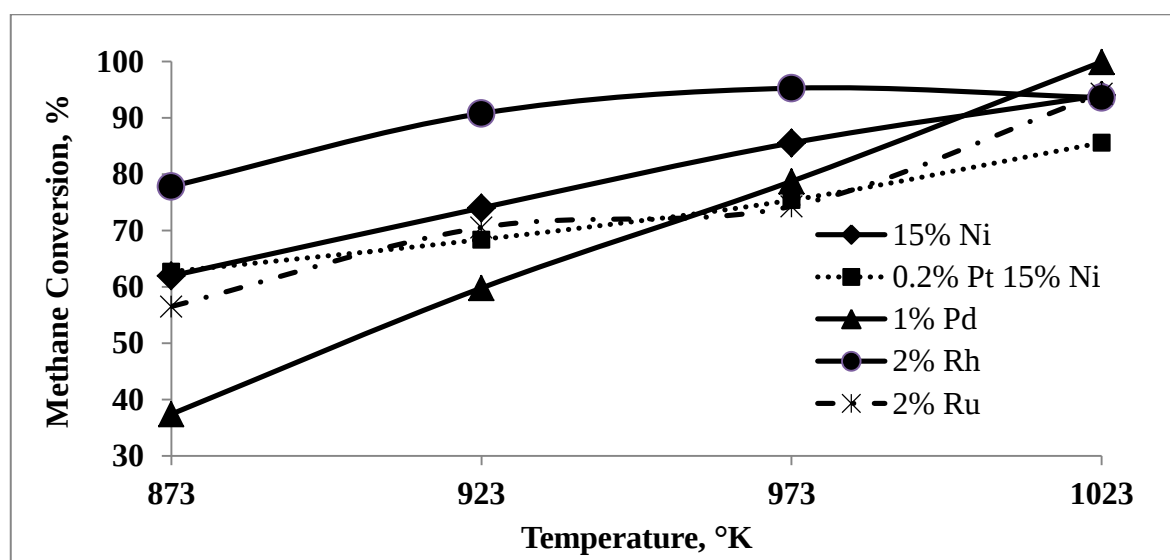


Figure 4.11. Effect of temperature on methane conversion over δ - Al_2O_3 supported catalysts reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$ with $S/C = 2.5$.

Figure 4.12 shows the effect of temperature on the H_2/CO ratios obtained over different catalysts. Higher H_2/CO ratios (>3.0) were obtained at lower temperatures, indicating that H_2 production was favored, while H_2/CO ratios ≤ 3.0 , more suitable for synthesis gas production, were achieved at temperatures above 973 K. At lower temperatures, the contribution of the water gas shift (WGS) reaction is significant in supporting MSR, while at higher reaction temperatures it is likely that the reverse WGS reaction becomes more prominent, consuming some of the hydrogen formed and increasing the amount of CO in the product.

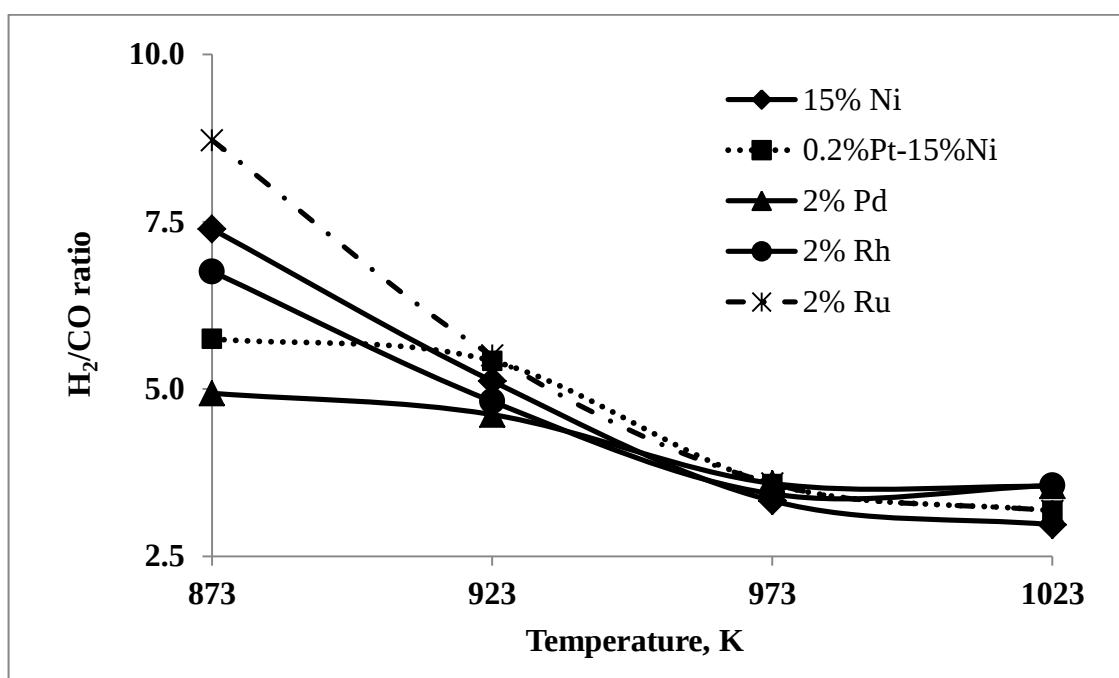


Figure 4.12. Effect of temperature on H_2/CO over $\delta-Al_2O_3$ supported catalysts reduced at 1073 K for 2h, $F_{total} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$ with $S/C = 2.5$.

4.1.6. Effect of Inlet Steam-to-Carbon Molar Ratio

The effect of the inlet S/C molar ratio was studied over 15%Ni/ $\delta-Al_2O_3$ and 0.2%Pt-15%Ni/ $\delta-Al_2O_3$ catalysts for assessing their MSR activity at ratios of 2.0-3.5 and temperature of 973 and 1023 K. Both CH_4 conversions and H_2/CO ratios were found to increase with increasing inlet S/C ratio, the major effect being observed in methane conversion over 15%Ni/ $\delta-Al_2O_3$ at 973 K, which also yields the highest H_2/CO ratios in the product stream. According to Le Chatelier's principle, excess steam favors water-gas shift reaction in the products direction, which converts CO generated by MSR into H_2 and CO_2 , and leads to higher H_2/CO ratios. In order to avoid coking in MSR, the recommended S/C molar ratio is around 2.5 which is above the stoichiometric ratios for CO or CO_2 forming MSR reactions (Rostrup-Nielsen, 1984).

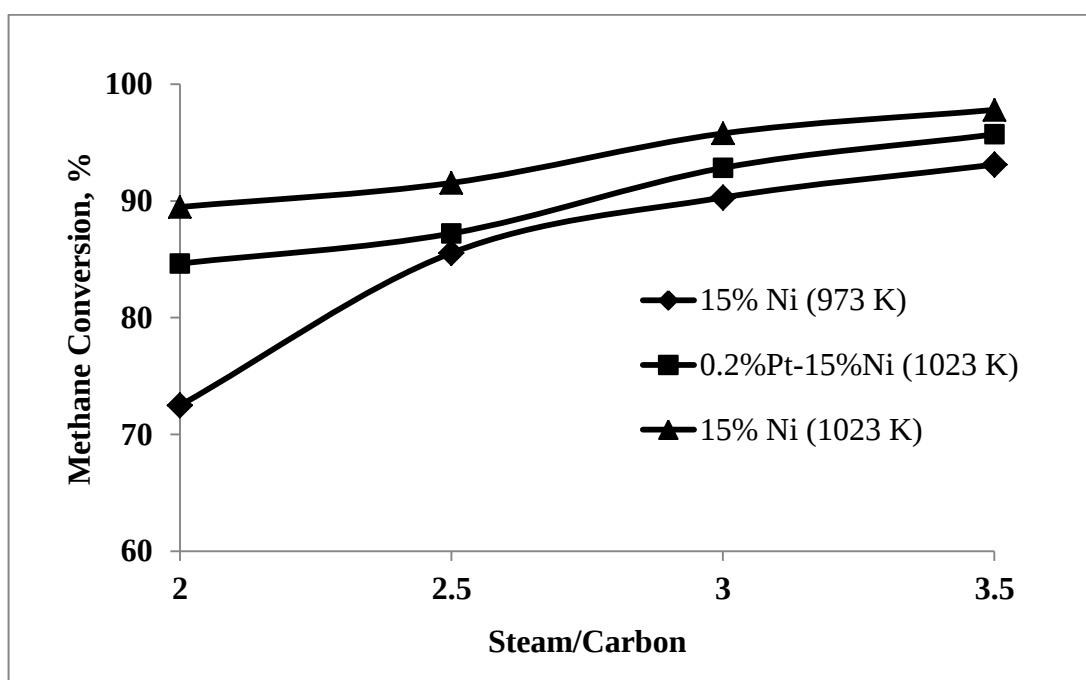


Figure 4.13. Effect of S/C on methane conversion over δ - Al_2O_3 supported catalysts reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$.

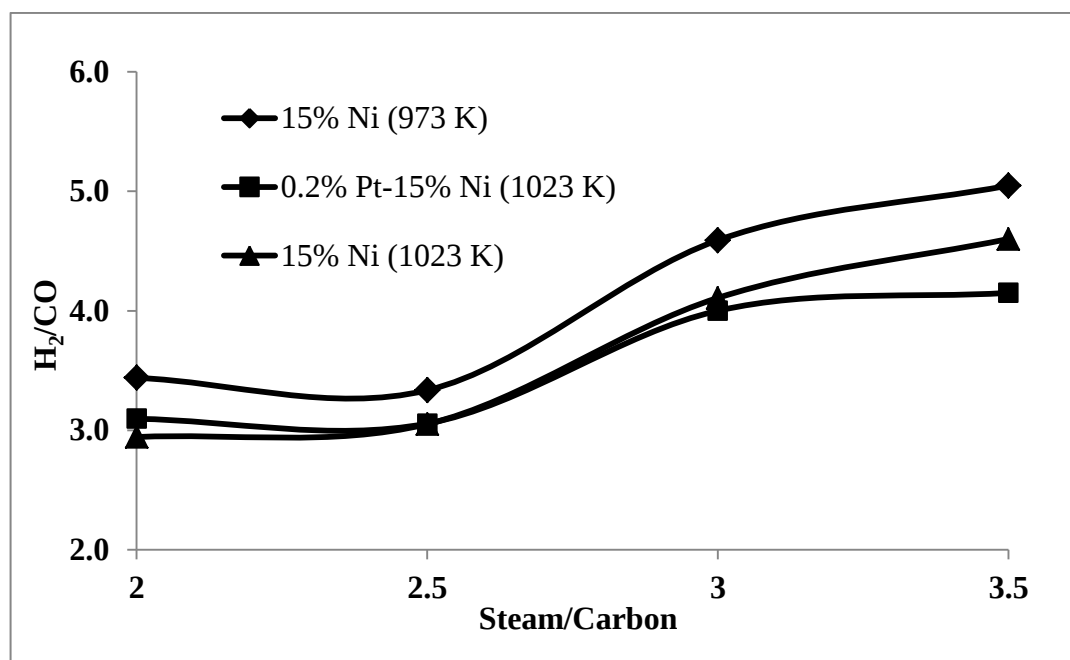


Figure 4.14. Effect of S/C on H_2/CO over δ - Al_2O_3 supported catalysts reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$.

4.1.7. Effect of 10% CO₂ in the Feed

Synthesis gas generation from methane for purposes of Fischer-Tropsch synthesis (FTS) normally requires a H₂/CO ratio of 2 at the FT reactor inlet; hence, the aim of MSR may also be to obtain a product stream with H₂/CO = 2. Therefore, the addition of 10% CO₂ into the MSR feed was studied to see its effect on methane conversion and molar H₂/CO ratios in the product over various catalysts including Ni/ δ -Al₂O₃, Pt-Ni/ δ -Al₂O₃, Pd/ δ -Al₂O₃, Rh/ δ -Al₂O₃ and Ru/ δ -Al₂O₃, at 873, 923, 973 and 1023 K. As in other experiments, the composition of the feed was fixed at CH₄/H₂O/CO₂/N₂:10/25/10/55 by volume in testing the effects of temperature. Figure 4.15 shows that over all catalysts, methane conversion rises with temperature. 2% Ru catalyst is most significantly affected by the addition of CO₂. The highest conversion reached is 99% over both Ni and Rh-based catalysts at 1023 K. At the same time, these two catalysts give relatively higher conversions even at lower temperature. On the other hand, the H₂/CO ratio decreases with increasing temperature on all catalysts (Figure 4.16), as expected on the basis of CO₂ free MSR results. The desirable H₂/CO ratio of 2 is in fact reached above 973 K over all catalysts, except 2%Ru/ δ -Al₂O₃.

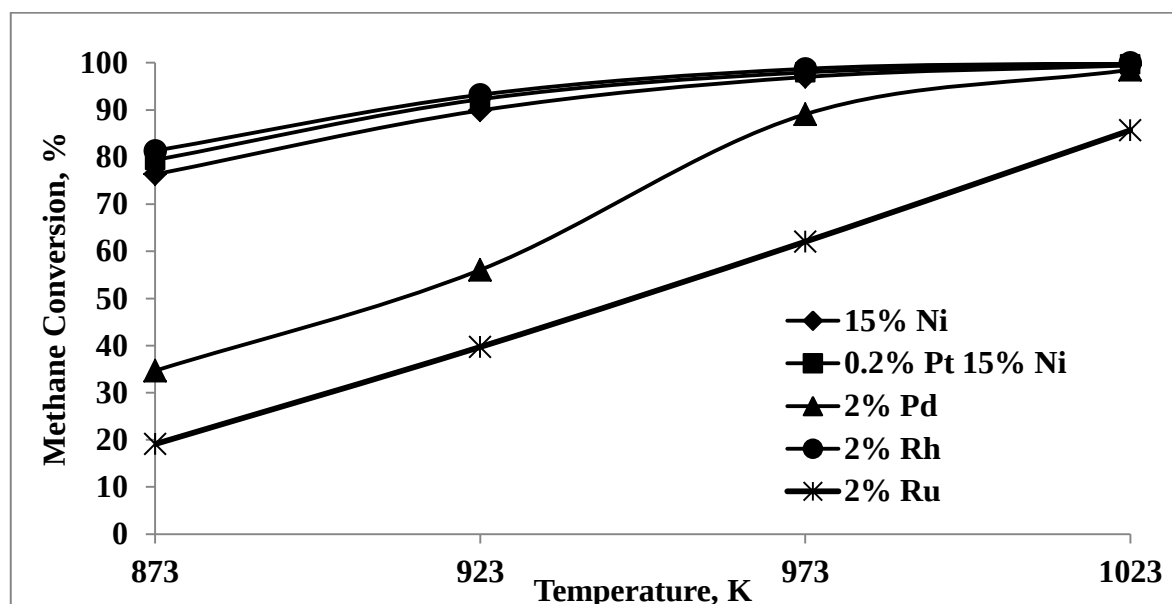


Figure 4.15. Effect of temperature on methane conversion over δ -Al₂O₃ supported catalysts at reduced 1073 K for 2h, $F_{\text{total}}=150 \text{ cm}^3 \cdot \text{min}^{-1}$, CH₄/H₂O/CO₂/N₂:10/25/10/55.

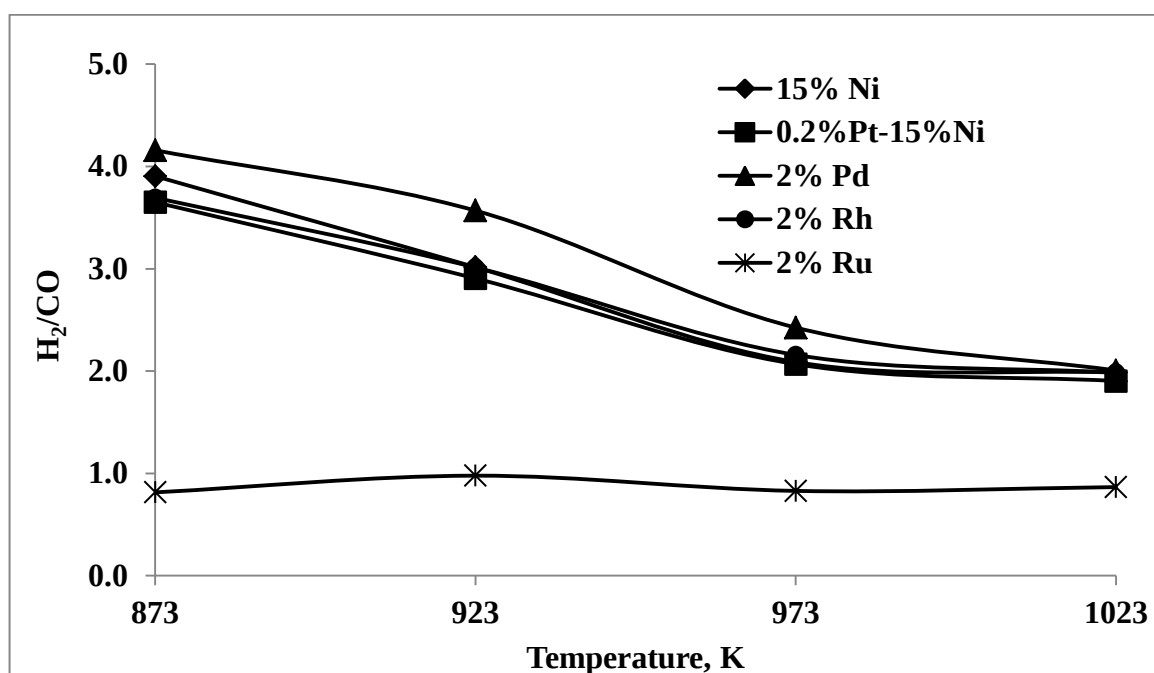


Figure 4.16. Effect of temperature on H_2/CO over $\delta\text{-Al}_2\text{O}_3$ supported catalysts reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, $\text{CH}_4/\text{H}_2\text{O}/\text{CO}_2/\text{N}_2$:10/25/10/55.

In Figures 4.17-20, the effects of the presence of CO_2 in the feed on methane conversion and the product H_2/CO ratio are presented for each catalyst. The difference from the experiments in which there is no CO_2 in the feed is that lower methane conversions are obtained over all catalysts. Presence of CO_2 in the feed clearly decreases methane conversion due to the fact that the higher CO_2 concentration in the reaction mixture supports the reverse WGS and possibly the methanation reactions. Unlike other catalysts, methane conversions over $\text{Pd}/\delta\text{-Al}_2\text{O}_3$ and $\text{Rh}/\delta\text{-Al}_2\text{O}_3$ catalysts are not affected by the CO_2 addition due to lower WGS and methanation activity of these catalysts.

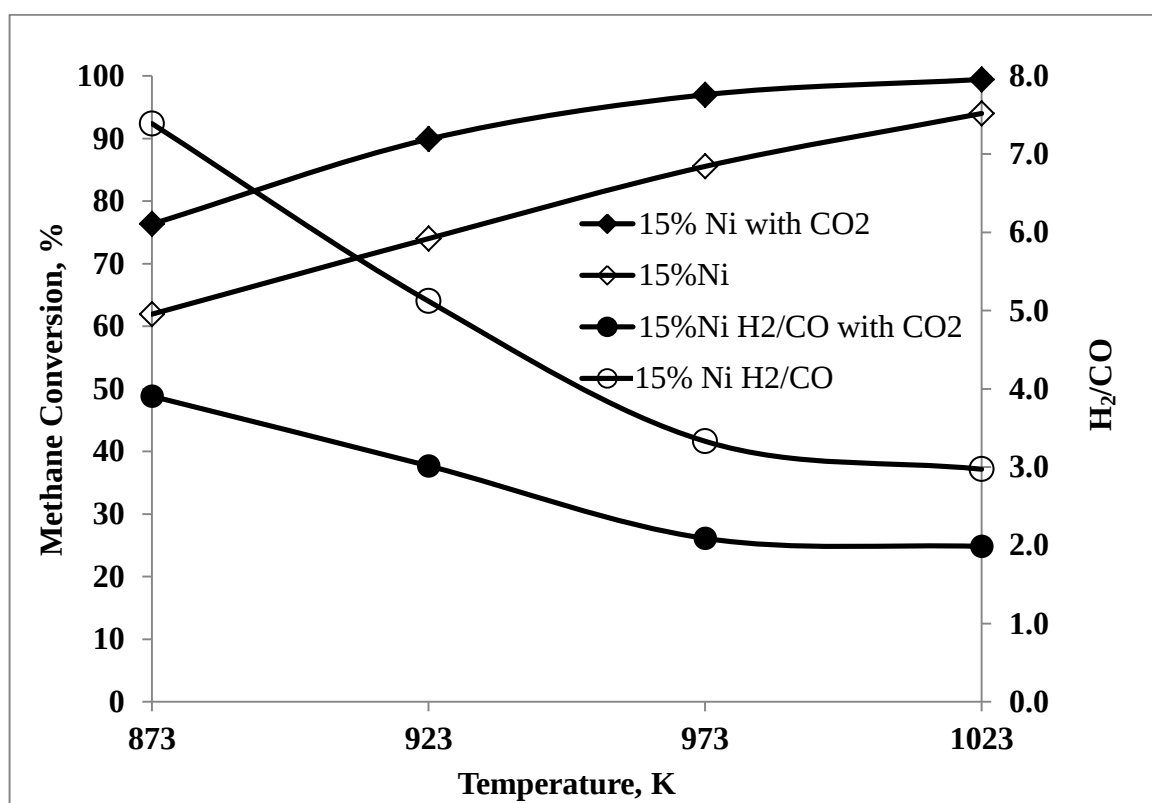


Figure 4.17. Effect of CO₂ addition to the feed on 15%Ni/δ-Al₂O₃, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, CH₄/H₂O/CO₂/N₂:10/25/10/55.

Evaluating the product H₂/CO ratios obtained in the presence of CO₂, it can be seen from the Figures 4.17-20 that it decreases for all the catalysts studied. Again, this stems from the fact that higher CO₂ concentrations prevent the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) from going forward. It is noteworthy that in the presence of CO₂, H₂/CO of 1 was obtained from 2%Ru/δ-Al₂O₃ catalyst (Figure 4.20), independently from temperature; therefore, it can safely be said that 2%Ru/δ-Al₂O₃ is more sensitive to CO₂ concentration than to temperature.

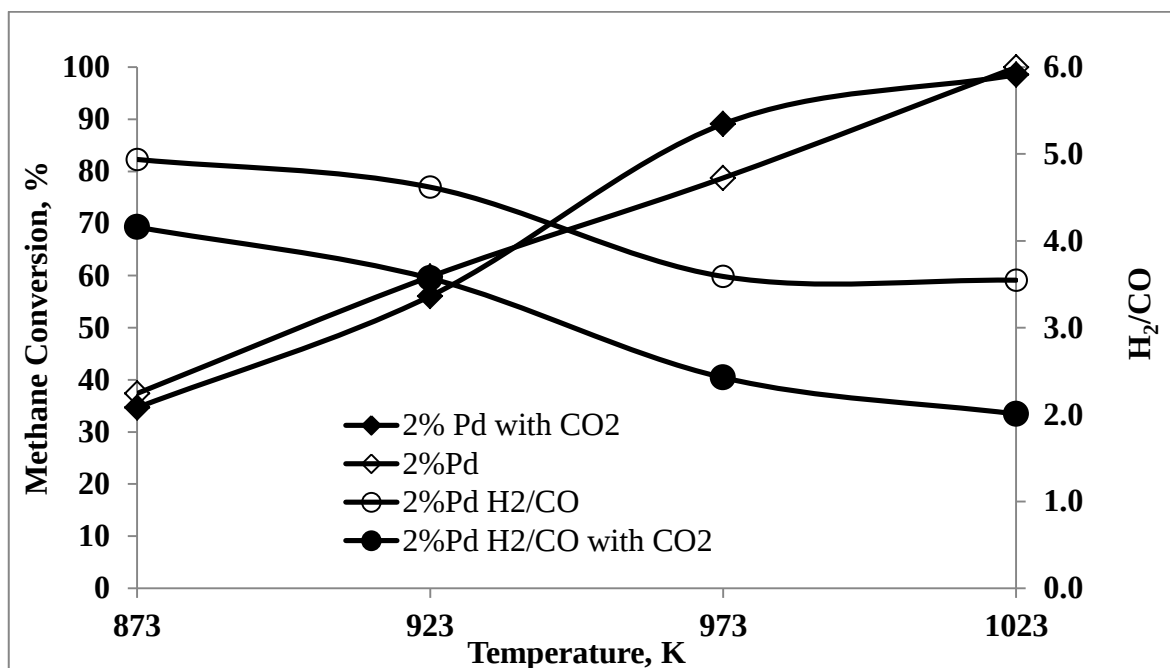


Figure 4.18. Effect of CO₂ addition to the feed on 2%Pd/δ-Al₂O₃, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, CH₄/H₂O/CO₂/N₂:10/25/10/55.

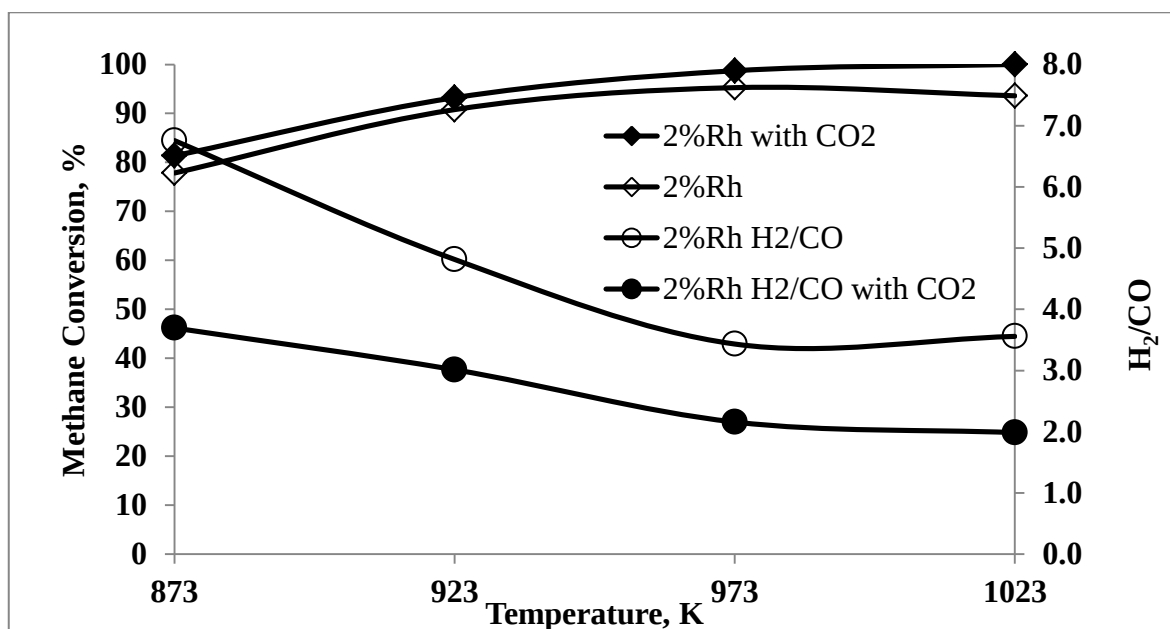


Figure 4.19. Effect of CO₂ addition to the feed on 2%Rh/δ-Al₂O₃, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, CH₄/H₂O/CO₂/N₂:10/25/10/55.

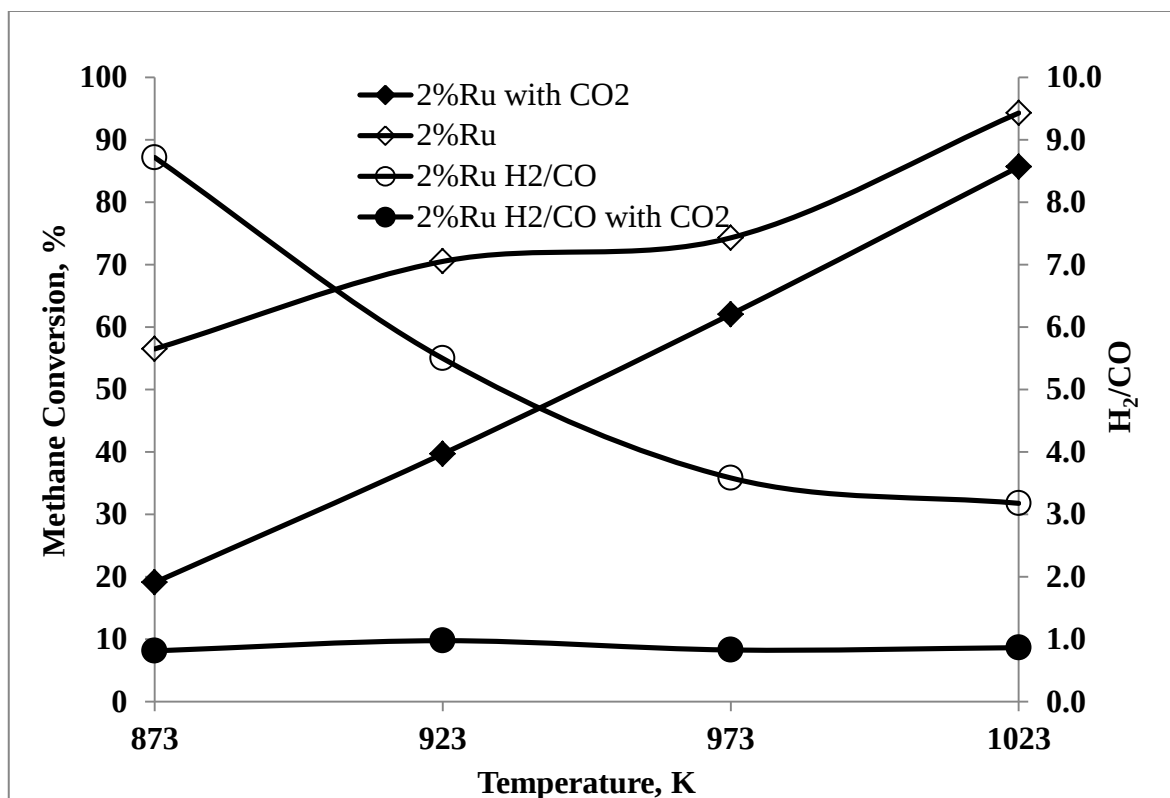


Figure 4.20. Effect of CO₂ addition to the feed on 2%Ru/ δ -Al₂O₃, reduced at 1073 K for 2h, $F_{\text{total}} = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, CH₄/H₂O/CO₂/N₂:10/25/10/55.

The following conclusions can be drawn on the basis of the work conducted in the conventional packed-bed microreactor for assessing MSR activities of Ni/ δ -Al₂O₃, Pt-Ni/ δ -Al₂O₃, Pd/ δ -Al₂O₃, Rh/ δ -Al₂O₃ and Ru/ δ -Al₂O₃: Ni sites (i) almost cover the δ -Al₂O₃ surface, and (ii) are dispersed homogenously. In addition, as indicated by EDX analysis, the impregnated Ni content in catalyst is 14.84% in parallel with the targeted amount of 15%.

- Methane conversion decreases with increasing catalyst particle size indicating the existence of internal mass transport resistances in larger particles. In order to eliminate internal transport resistances, catalytic activity tests are conducted with average particle size 300 μm .

- Rh-based catalyst is distinguished from others in that it is quite not affected by temperature changes in the 873-1023 K range and exhibits higher CH₄ conversions even at the lower temperatures.
- At the highest temperature tested, 1023 K, all catalysts exhibit similar conversions close to the equilibrium conversion level.
- Both methane conversions and product H₂/CO ratios are found to increase with increasing S/C molar ratio in the feed.
- In the presence of 10% CO₂ in the feed, methane conversion increases with temperature over all catalysts tested; the highest CH₄ conversion reached is 99% over Ni and Rh based catalysts at 1023 K.
- Unlike the other catalysts, methane conversions over Pd/ δ -Al₂O₃ and Rh/ δ -Al₂O₃ catalysts are not affected by the CO₂ addition due to lower WGS and methanation activity of these catalysts

4.2. MSR in Packed and Coated Microchannel Reactors (MCR)

The major aim of this part of the study is 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. Methane steam reforming experiments 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 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 carbon (or methane) at the inlet.

4.2.1. 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 -Al₂O₃ 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 4.1, while representative ESEM images of 2% precious metal containing catalysts are shown in Figures 4.21-24, together with the cross-sectional image of the coated catalyst layer obtained in preparing the 2% Rh catalyst. EDX mapping results clearly indicate uniform metal dispersion, and actual metal loadings quite close to the targeted values for all catalysts (Table 4.1). The cross-sectional ESEM image of freshly coated 2% Rh/ δ -Al₂O₃ layer is representative of the uniform catalyst layer thickness attained in the preparation of each coated catalyst.

Table 4.1. Targeted and achieved metal loadings of particulate and coated catalysts obtained from EDX mapping analyses.

Catalyst	Target metal loading (wt%)	Actual metal loading Coated form (wt%)	Actual metal loading Particulate form (wt%)
Rh/ δ -Al ₂ O ₃	2	1.97	1.99
Ru/ δ -Al ₂ O ₃	2	2.11	2.52
Pd/ δ -Al ₂ O ₃	2	2.50	2.27
Ni/ δ -Al ₂ O ₃	10	8.29	10.13

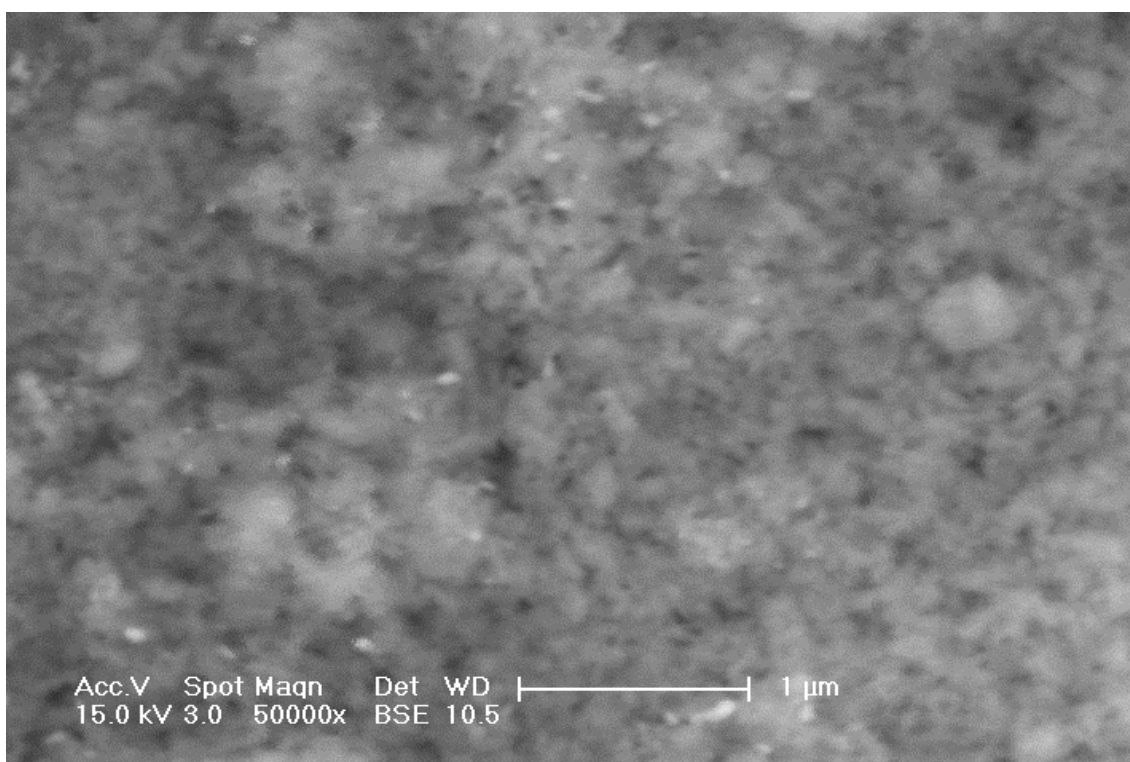


Figure 4.21. ESEM micrographs (50000×) of 2%Rh/δ-Al₂O₃.

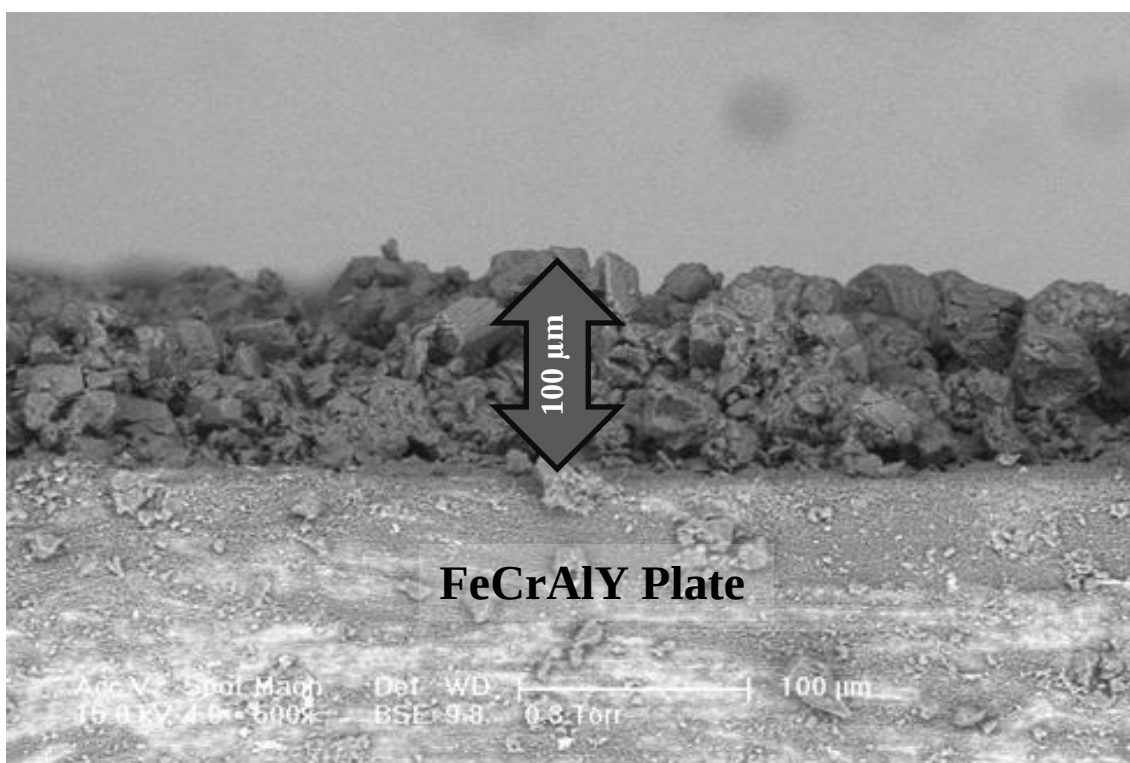


Figure 4.22. ESEM micrographs (50000×) of 2%Rh/δ-Al₂O₃.

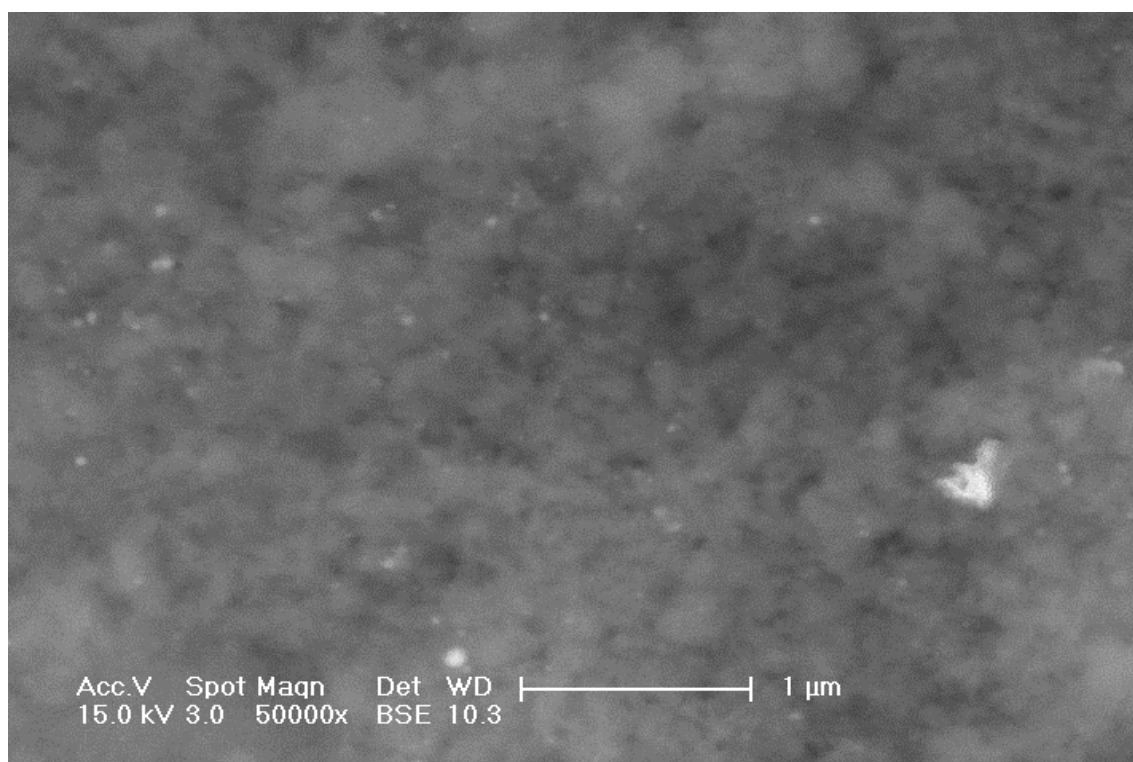


Figure 4.23. ESEM micrographs (50000×) of 2%Pd/δ-Al₂O₃.

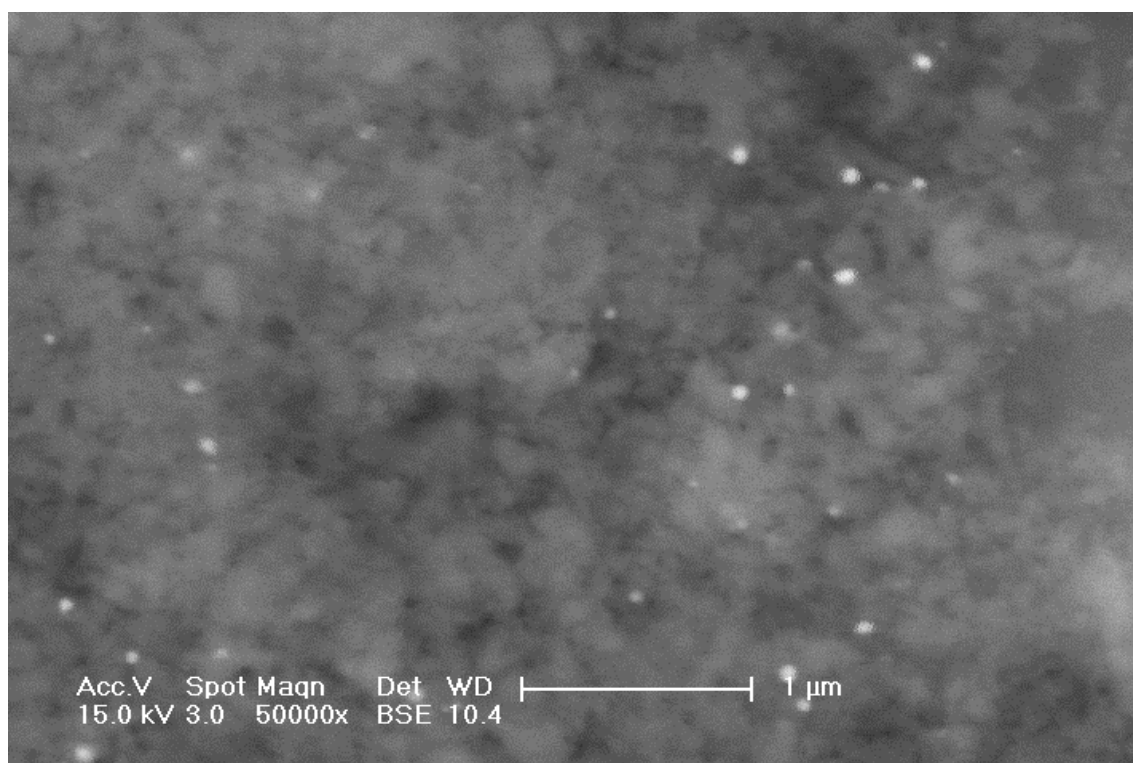


Figure 4.24. ESEM micrographs (50000×) of 2%Ru/δ-Al₂O₃.

The X-ray diffraction (XRD) patterns of plates coated with Ni/ δ -Al₂O₃ catalyst after calcination, reduction and reaction steps (Figure 4.25) were reported by Karakaya *et al.* (2012). At high calcination temperatures (ca. 1173 K), a large portion of the Ni impregnated onto δ -Al₂O₃ transforms into the NiAl₂O₄ spinel phase which is difficult to activate due to its stability (Jeong *et al.*, 2006). Since calcination in this work is carried out at 873 K, spinel peaks are not detected. The reduction temperature, on the other hand, is set as 1073 K because at temperatures below 973 K, Ni/ δ -Al₂O₃ catalysts cannot be reduced appreciably, and thus, cannot be properly activated (Aartun *et al.*, 2005). Upon reduction, metal oxides are reduced to metallic Ni.

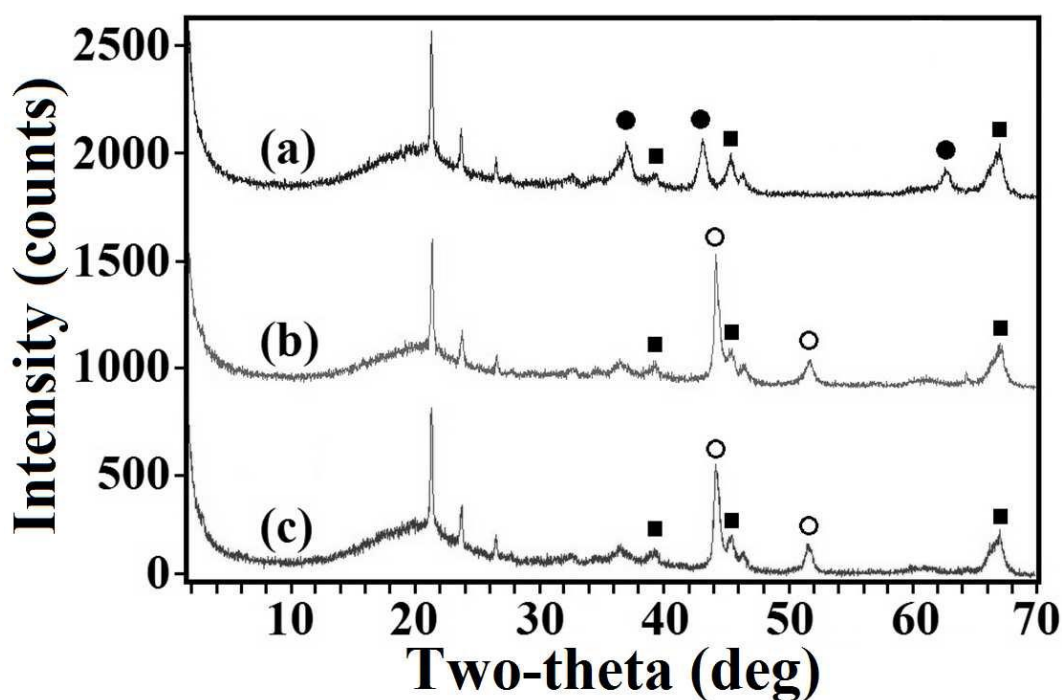


Figure 4.25. XRD patterns for the (a) calcined, (b) calcined and reduced, (c) calcined, reduced and reacted Ni catalysts coated on plates ((■)Al₂O₃, (●) NiO, (○) NiO) (Karakaya, *et al.*, 2012).

4.2.2. 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 $W/F_{\text{CH}_4,0}$ ratio constant at the same value of $7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ 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.

4.2.3. 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 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 $7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$ 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 (Rostrup-Nielsen, 1984). 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 $W_{\text{cat}}/F_{\text{CH}_4,0}$ ratio selected ($7.22 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$) 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 Figure 4.26 together with the corresponding

equilibrium conversion levels calculated from thermodynamic data using the 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.

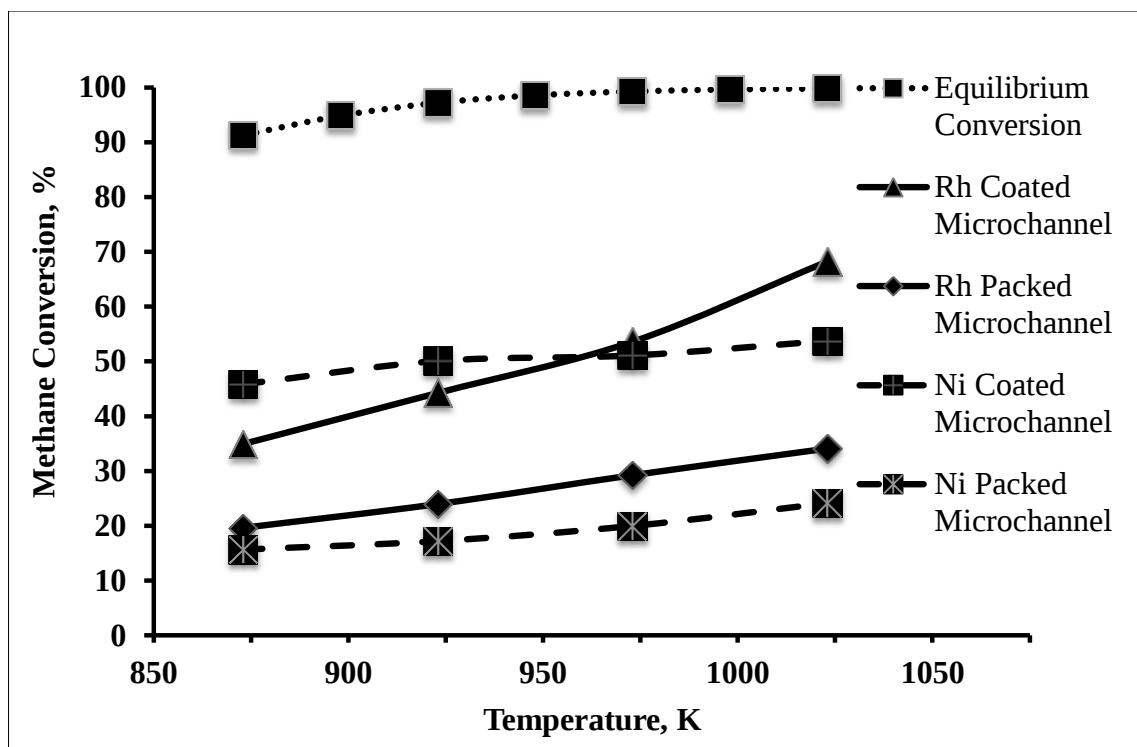


Figure 4.26. Effect of temperature on methane conversions obtained at $S/C = 2.5$ over 2wt% Rh and 10wt% Ni catalysts in coated and packed microchannel configurations and on corresponding equilibrium conversions.

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 Tables 4.2-3 and Figures 4.27-30. In each case, methane conversion increases with temperature, and conversions are highest over Rh at all temperatures; at 1023 K, methane 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 H₂ 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.

Table 4.2. Effect of reaction temperature on CH₄ conversion (X_{CH_4}), molar H₂/CO ratio in product, and production rates of H₂ (r_{H_2}) and CO (r_{CO}) in packed and coated microchannel reactors.

#	Catalyst	Temp. K	X_{CH_4} , %	H ₂ /CO	r_{H_2} , μmol/(min.mg)	r_{CO} , μmol/(min.mg)
1	2%Rh/δ-Al ₂ O ₃	873	19.6	15.4	3.77	0.24
2		923	23.9	9.7	4.22	0.44
3		973	29.3	7.1	4.88	0.69
4		1023	34.1	6.1	5.80	0.96
5	2%Ru/δ-Al ₂ O ₃	873	10.4	12.8	1.46	0.11
6		923	13.4	7.7	1.85	0.24
7		973	14.1	7.3	2.05	0.28
8		1023	15.8	7.3	2.24	0.31
9	2%Pd/δ-Al ₂ O ₃	873	12.2	11.8	1.99	0.17
10		923	16.7	7.1	2.79	0.39
11		973	21.1	6.9	3.58	0.51
12		1023	25.5	5.6	4.28	0.76
13	10%Ni/δ-Al ₂ O ₃	873	15.7	27.3	2.29	0.08
14		923	17.2	14.0	2.55	0.18
15		973	19.9	10.8	2.93	0.27
16		1023	24.2	8.4	3.5	0.42

Table 4.3. Effect of reaction temperature on CH₄ conversion (X_{CH_4}), molar H₂/CO ratio in product, and production rates of H₂ (r_{H_2}) and CO (r_{CO}) in coated microchannel reactors.

#	Catalyst	Temp. K	X_{CH_4} , %	H ₂ /CO	r_{H_2} , $\mu\text{mol}/(\text{min.mg})$	r_{CO} , $\mu\text{mol}/(\text{min.mg})$
1	2%Rh/ δ -Al ₂ O ₃	873	34.9	5.9	5.90	1.00
2		923	44.2	4.4	7.39	1.69
3		973	53.6	4.1	8.97	2.17
4		1023	68.2	3.4	11.31	3.32
5	2%Ru/ δ -Al ₂ O ₃	873	31.32	8.1	5.41	0.67
6		923	35.9	5.9	6.10	1.03
7		973	38.7	5.6	6.70	1.20
8		1023	38.8	5.2	7.69	1.48
9	2%Pd/ δ -Al ₂ O ₃	873	28.8	5.8	4.29	0.74
10		923	41.9	4.6	6.62	1.43
11		973	55.1	4.5	8.38	1.85
12		1023	55.9	4.6	9.08	1.98
13	10%Ni/ δ -Al ₂ O ₃	873	45.8	10.4	7.61	0.73
14		923	50.1	7.4	8.03	1.09
15		973	51.1	6.7	8.53	1.28
16		1023	53.8	6.0	8.42	1.41

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, with deviations becoming more significant at low temperatures. These observations indicate the effect of the exothermic water-gas shift, an important side reaction (Rostrup-Nielsen, 1984), 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 water-gas shift reaction 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. 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 4.2-3).

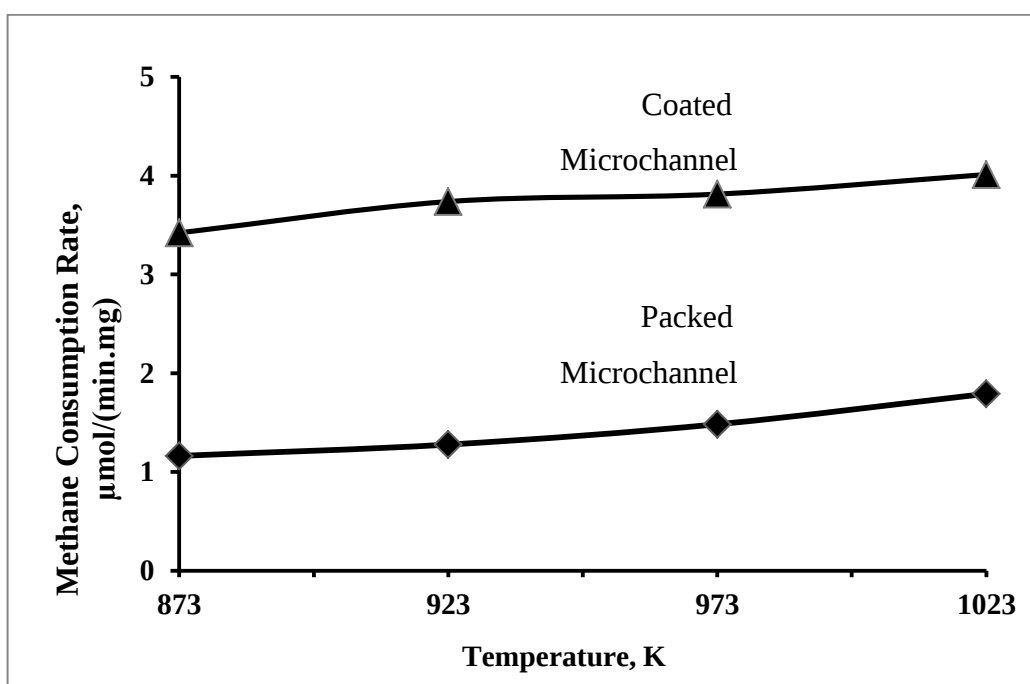


Figure 4.27. Effect of temperature on methane consumption rates at $S/C = 2.5$ over $10\%Ni/\delta-Al_2O_3$ catalysts in coated and packed microchannel reactors.

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.

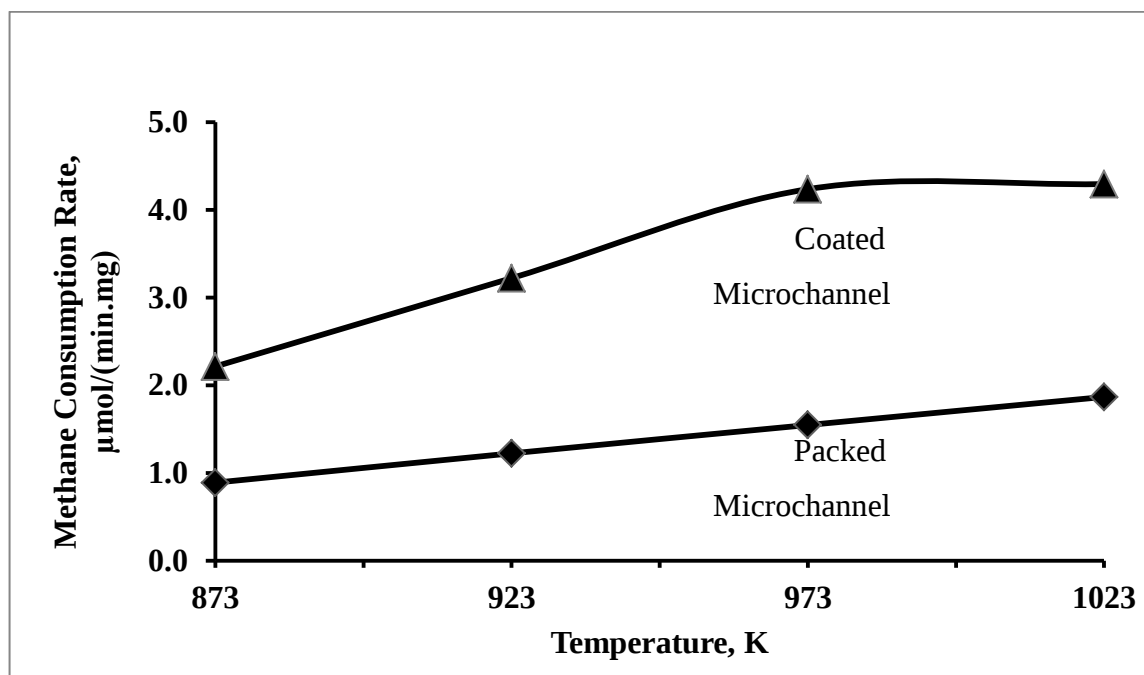


Figure 4.28. Effect of temperature on methane consumption rates at S/C= 2.5 over 2%Pd/δ-Al₂O₃ catalysts in coated and packed microchannel reactors.

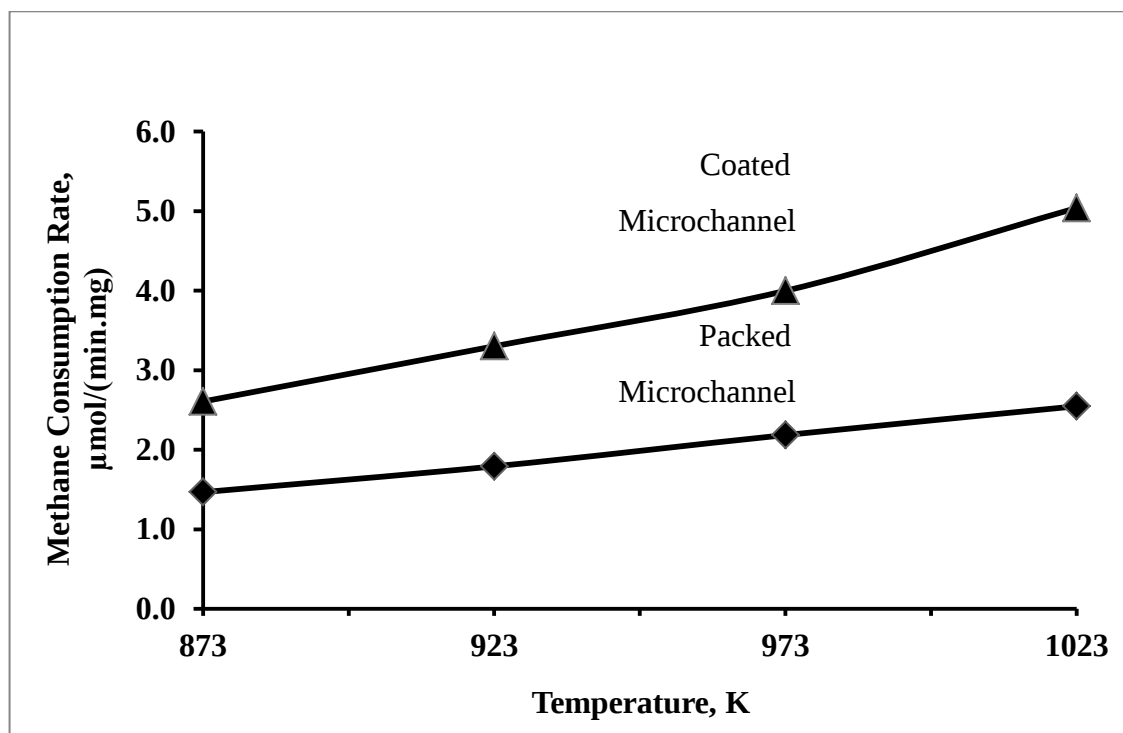


Figure 4.29. Effect of temperature on methane consumption rates at S/C= 2.5 over 2%Rh/δ-Al₂O₃ catalysts in coated and packed microchannel reactors.

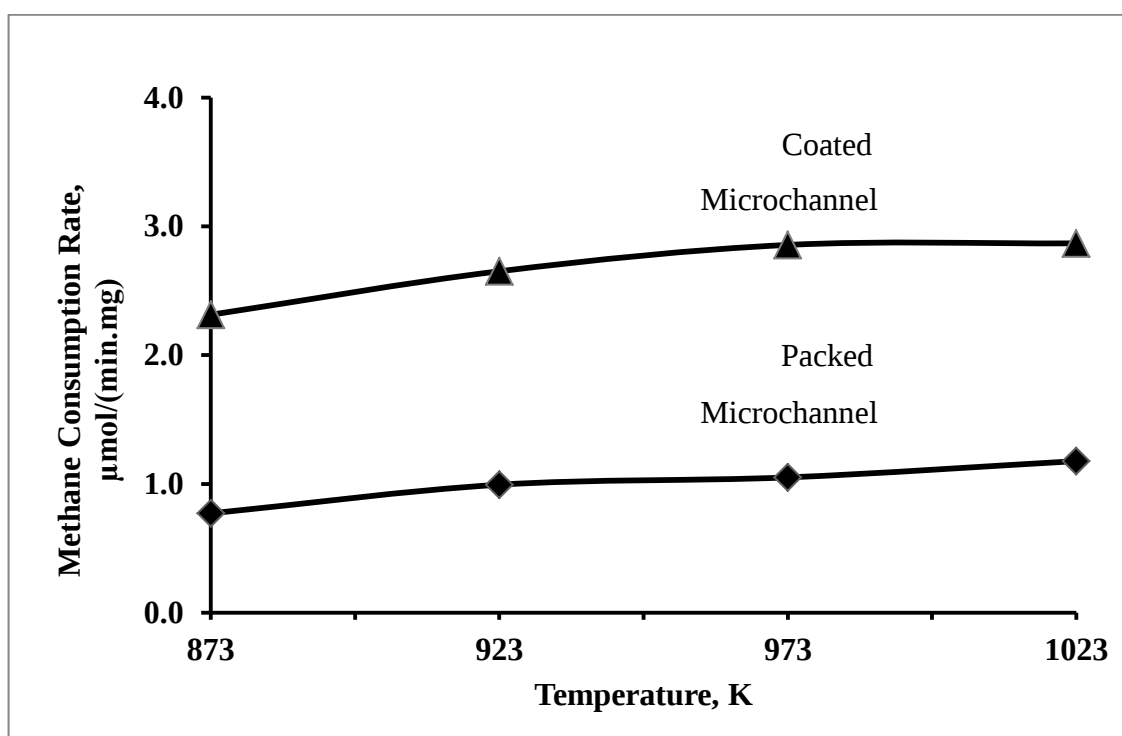


Figure 4.30. Effect of temperature on methane consumption rates at S/C= 2.5 over 2%Ru/ δ -Al₂O₃ catalysts in coated and packed microchannel reactors.

4.2.4. 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 packed and coated microchannel reactors are summarized and compared in Tables 4.4-5, respectively. 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. Highest 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.

Table 4.4. Effect of inlet steam-to-carbon molar ratio (S/C) on methane conversion (X_{CH_4}), molar H_2/CO ratio in product, methane consumption rate ($-r_{CH_4}$) and production rates of H_2 (r_{H_2}) and CO (r_{CO}) in packed microchannel reactors.

#	Catalyst	S/C	X_{CH_4} , %	H_2/CO	$-r_{CH_4}$, $\mu\text{mol}/$ (min.mg)	r_{H_2} , $\mu\text{mol}/$ (min.mg)	r_{CO} , $\mu\text{mol}/$ (min.mg)
1	2%Rh/ δ - Al_2O_3	2.5	34.1	6.07	2.55	5.80	0.96
2		3	33.5	6.33	2.67	6.26	0.99
3		3.5	35.3	6.66	3.10	6.68	1.00
4	2%Ru/ δ - Al_2O_3	2.5	15.8	7.31	1.18	2.24	0.31
5		3	18.2	7.26	1.45	2.50	0.34
6		3.5	20.8	7.47	1.81	2.85	0.38
7	2%Pd/ δ - Al_2O_3	2.5	25.5	5.61	1.87	4.28	0.76
8		3	36.9	7.33	2.72	3.30	0.45
9		3.5	38.7	8.04	3.12	3.69	0.46
10	10%Ni/ δ - Al_2O_3	2.5	24.2	8.38	1.79	3.55	0.42
11		3	23.9	8.92	1.91	3.95	0.44
12		3.5	26.2	9.16	2.30	4.09	0.45

The overall increase in the H_2/CO molar ratio in the product stream has the following trend: 2% Rh < 2% Pd $\leq$ 2% Ru < 10% Ni in packed microchannels, which is slightly

modified in coated microchannels as $2\% \text{ Rh} < 2\% \text{ Pd} < 2\% \text{ Ru} \leq 10\% \text{ Ni}$. 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.

Table 4.5. Effect of inlet steam-to-carbon molar ratio (S/C) on methane conversion (X_{CH_4}), molar H_2/CO ratio in product, methane consumption rate ($-r_{\text{CH}_4}$) and production rates of H_2 (r_{H_2}) and CO (r_{CO}) in coated microchannel reactors.

#	Catalyst	S/C	X_{CH_4} , %	H_2/CO	$-r_{\text{CH}_4}$, $\mu\text{mol}/$ (min.mg)	r_{H_2} , $\mu\text{mol}/$ (min.mg)	r_{CO} , $\mu\text{mol}/$ (min.mg)
	2%Rh/ δ - Al_2O_3	2.5	68.2	3.41	5.04	11.31	3.32
		3	71.6	4.03	5.71	12.53	3.11
		3.5	72.7	4.21	6.39	13.34	3.17
	2%Ru/ δ - Al_2O_3	2.5	38.8	5.2	2.87	7.69	1.48
		3	37.6	6.36	2.94	6.99	1.10
		3.5	46.4	5.07	3.87	8.34	1.64
	2%Pd/ δ - Al_2O_3	2.5	55.9	4.60	4.29	9.08	1.98
		3	55.2	4.88	4.41	9.42	1.93
		3.5	56.6	5.04	4.69	10.09	2.00
	10%Ni/ δ - Al_2O_3	2.5	53.8	5.99	4.01	8.42	1.41
		3	53.9	6.28	4.17	9.25	1.47
		3.5	55.2	6.88	4.60	9.91	1.44

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 2wt% Rh, 2wt% Ru, 2wt% Pd, and 10wt% 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 H₂ 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, H₂ and CO production rates over 2wt% Rh were the highest. It was found that the H₂/CO molar ratios in coated microchannel product streams are significantly lower than those in packed microchannels, 2wt% Rh is better in terms of CO selectivity while 10wt% Ni gives the highest H₂ selectivity. These results indicate the possibility of reducing H₂/CO ratio in MSR by using wall-coated microchannel reformers.

4.3. OSR of Methane in Packed Microchannel Reactors (MCR)

Studies on oxidative steam reforming of methane (OSRM) in microchannel reactors were conducted by changing one parameter at a time while keeping all others constant. The aim of this part of the work was to compare the OSRM performances of two typical microchannel reactor configurations – packed and wall-coated– that are operated under identical conditions in terms of a wide range of parameter values including residence time, reaction temperature, inlet steam-to-carbon (S/C) and oxygen-to-carbon (O₂/C) molar ratios. Experiments were carried out within a wide test matrix and involved testing of δ -Al₂O₃ supported 0.2wt%Pt-2wtRh catalyst at different temperatures, steam-to-carbon ratios, oxygen-to-carbon ratios and residence time through a parametric approach. OSRM experiments in packed-bed micro-channels were conducted within the scope of this dissertation, while those in coated microchannel reactors were performed by Karakaya under the same conditions (Karakaya, 2012). The equilibrium compositions for the product mixtures were calculated for each case by using the HSC 6.1 Chemistry software via the Gibbs free energy minimization method, which also included the possible formation of solid carbon. The experimental conditions were selected so as to guarantee conversions

below the equilibrium values for better comparison of catalyst activity and selectivity toward products in different cases.

OSRM experiments are carried out at 773, 823, 873 and 923 K and at atmospheric pressure with steam-to-carbon-ratios of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, and oxygen-to-carbon ratios of 0.0, 0.47, 0.54 and 0.63, using weight-based contact times of 0.35, 0.41, 0.50 and 0.71 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$.

4.3.1. Effect of Reaction Temperature

The effect of reaction temperature on methane conversion and CO selectivity obtained over coated and packed microchannel configurations are reported in Figures 4.31-32. The feed composition is kept constant at an inlet methane concentration of 14.3% (by mole). S/C and O_2/C molar ratios of 3.0 and 0.47, respectively, and contact time of 0.36 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$ are used in the experiments. It can be observed that, regardless of the microchannel geometry, methane conversion increased with temperature due to its positive effect on the reaction rates. The conversions are also similar quantitatively. Both reactor configurations delivered close values of methane conversions which are found to differ slightly (i.e. by ca. 5%) from each other, but stay significantly below the equilibrium limit ranging between 70-98% (Figure 4.31). This is due to operation at a very short residence time of 0.36 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$ (that corresponds to ca. 12.94 ms based on total microchannel volume including the catalyst) which is not sufficient for the contact of the reactants with the catalyst to yield higher conversions. Proximity of the packed and coated catalyst conversions, however, seems to be invalid for the CO selectivities (Figure 4.32). Although the rate of CO production, hence its selectivity, increases thermodynamically with temperature due to endothermic CO-producing SR ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$, $\Delta H^\circ = 206.2$ kJ/mol) and exothermic CO-consuming WGS ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, $\Delta H^\circ = -41.2$ kJ/mol) in both geometries, the sensitivity of the coated catalyst against temperature, which is notably higher than that of the packed counterpart, leads to a wider selectivity gap with temperature. Considering the similarity of methane conversions, the increasing difference in CO selectivities can be explained by the extent of WGS, which is thought to differ with the catalyst geometry. Even though the contact time ($W_{\text{cat}}/F_{\text{CH}_4,0}$), based on inlet methane flow, is kept the same in both geometries, its distribution is inherently wider in the packed-

bed configuration due to the random pattern of fluid flow. This allows part of the reactive mixture to spend more time on the catalyst and, hence, to increase the extent of WGS for competing with the increasing the SR-based CO production rate, leading to a slower increase of CO selectivity with temperature.

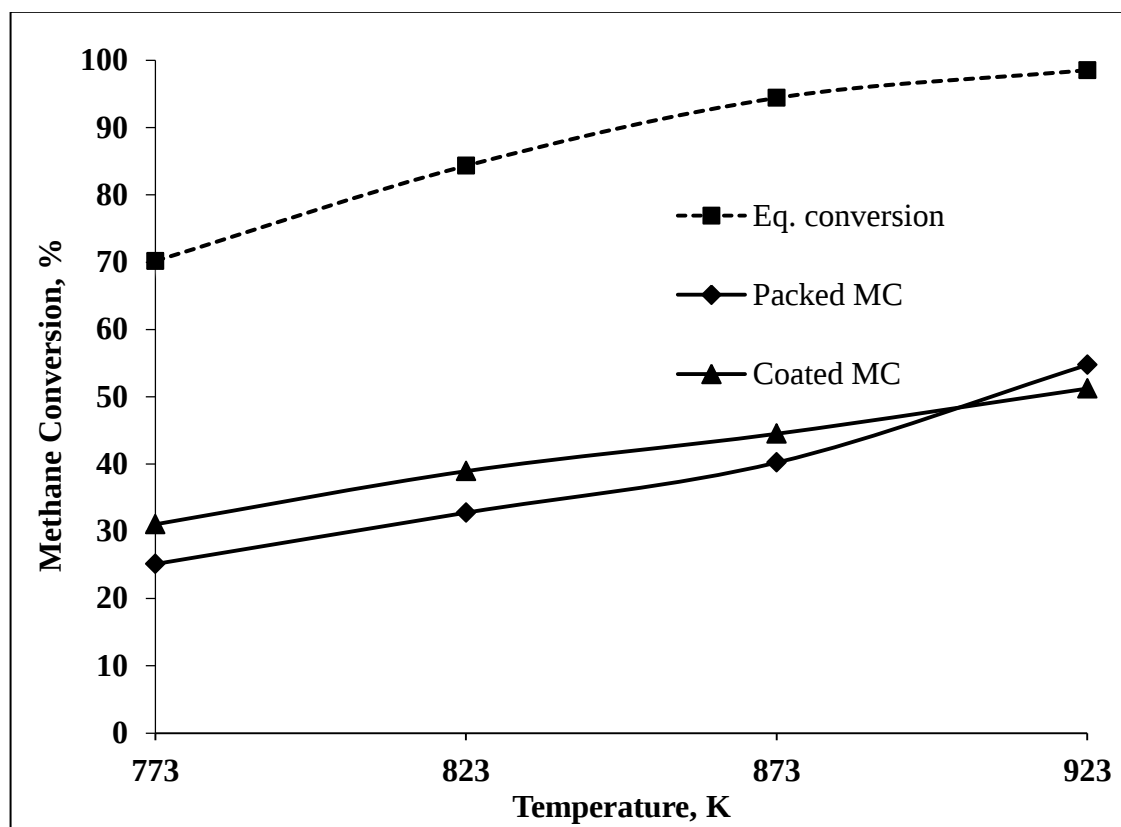


Figure 4.31. Effect of temperature on CH₄ conversions over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels and on equilibrium conversions (inlet CH₄= 14.3 mol%, S/C= 3.0, O₂/C= 0.47, W_{cat}/F_{CH₄,0}= 0.356 mg·min·cm⁻³).

Difference in the fluid flow pattern can also affect the mechanism through which methane is converted to syngas. It is reported that direct conversion of methane to syngas by partial oxidation (POX) is favored at short residence times and in the presence of monolith-supported Rh-based catalysts (Hickman and Schmidt, 1993; Vesper, 2008; Boucouvalas *et al.*, 1993):



These conditions are similar to those involved in the coated microchannel reactor that delivers higher CO selectivities through a well-defined catalytic flow path as in the case of monoliths. The possible presence of POX in the coated configuration can also be understood by the observation of rapid increase of CO selectivity with temperature which is known to favor the POX mechanism (Veser, 2008). On the other hand, SR is expected to be the main route of CO production in the packed microchannel that produces syngas with lower CO selectivity according to the stoichiometry of SR reaction ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$).

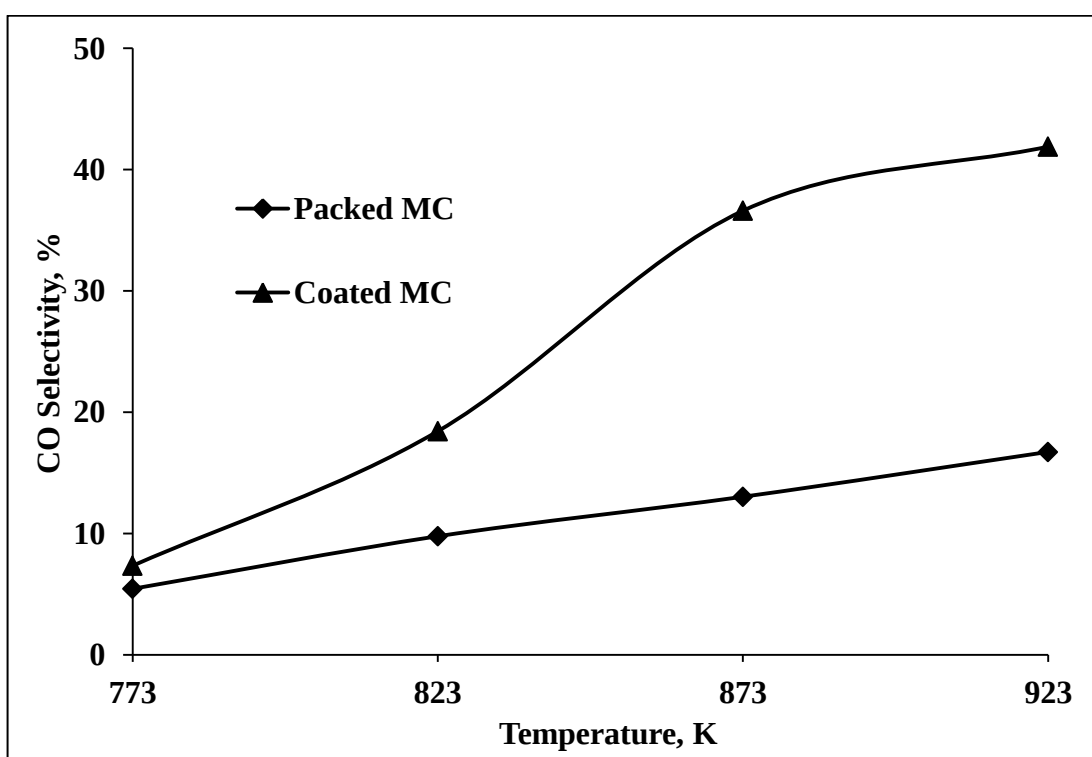


Figure 4.32. Effect of temperature on CO selectivity over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels (inlet $\text{CH}_4 = 14.3$ mol%, $\text{S/C} = 3.0$, $\text{O}_2/\text{C} = 0.47$, $W_{\text{cat}}/F_{\text{CH}_4,0} = 0.356 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$).

Table 4.6. H₂/CO ratio in product gas mixture over 0.2wt%Pt-2wt%Rh in packed and coated (*conducted by Karakaya, 2012) microchannel configurations.

Parameters		Hydrogen-to-CO ratio	
		Packed MC	Coated MC*
Tempetature (K)	773	6.47	1.73
	823	7.05	2.46
	873	7.16	2.17
	923	8.53	2.12
Steam-to-carbon ratio	0.0	2.88	1.04
	0.5	4.51	1.22
	1.0	4.77	1.52
	1.5	5.83	1.53
	2.0	6.47	1.52
	2.5	8.02	1.71
	3.0	8.53	2.12
Oxygen-to-carbon ratio	0.00	7.43	NA
	0.47	8.54	2.12
	0.54	7.64	2.1
	0.63	6.67	2.17
Contact time (mg·min·cm ⁻³)	0.71	9.34	2.9
	0.51	9.03	2.95
	0.41	8.81	2.40
	0.36	8.53	2.12

Composition of the synthesis gas, expressed in terms of molar H₂/CO ratio, is crucial in shaping up the product distribution obtained from the syngas fed processes such as Fischer-Tropsch synthesis. The impact of reaction temperature on H₂/CO ratio is given in Table 4.6. Owing to its higher CO selectivity, the coated microchannel delivered syngas ratios significantly below those obtained from the packed one. Moreover, temperature change led to different responses such that the syngas ratio continuously increased with

temperature in the packed configuration, whereas it decreased in the coated one operated in the 823-923 K range (Table 4.6). These differences can be attributed to the significance of different syngas production mechanisms, namely SR that produces H₂-rich syngas according to SR reaction ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$) in the packed geometry and POX, whose existence become detectable at higher temperatures to favor CO production in the coated microchannel. The local increase of syngas ratio from 1.74 to 2.47, obtained by a temperature shift from 773 K to 823 K in the coated configuration, can be explained by the fact that, at lower temperatures, H₂ production is thermodynamically favored over the CO production.

4.3.2. Effect of Inlet Steam-to-Carbon Molar Ratio

The effect of steam-to-carbon ratio on methane conversion and CO selectivity obtained over coated and packed microchannel configurations are shown in Figures 4.33-34. In these set of experiments, S/C is varied between 0 and 3.0, while O₂/C ratio, reaction temperature and contact time are kept constant at 0.47, 923 K and 0.36 mg.min.cm⁻³, respectively. In contrast with temperature, the effect of steam addition on methane conversion is found to be minimal. Increase in conversion against changing S/C from 0 to 3.0 is measured to be from 50.6% to 54.7% and from 45.5% to 51.2% in packed and coated microchannels, respectively. Even though the quantitative change is small in both configurations, the trends of conversion curves are somewhat different. In the packed microchannel, conversion increased from 50.6% to 55.7% when S/C changed from 0 to 0.5, but decreased monotonically to 52.1% in the S/C range of 0.5-2.5. On the other hand, conversion remained almost flat in the S/C range of 0-1.0, but constantly increased with further steam addition. The differences provide some hints about the way that syngas is produced. The trend in the packed configuration indicates the presence of SR, which responded rapidly by a small amount of steam addition according to SR reaction ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$). Considering the fact that extra steam is produced by methane total oxidation (TOX), the excess steam might have slightly inhibited SR as also reported in the literature (Rostrup-Nielsen, 1984):



A small, but positive move of conversion from 52.1% to 54.7% obtained by increasing S/C from 2.5 to 3.0 can be explained by a possible dominance of thermodynamics, which favors methane conversion by steam addition according to the Le Chatelier's principle. The flat zone in the coated configuration, however, pinpoints the likelihood of syngas production by some other mechanisms such as POX (Eq. 4.4). The increasing trend of conversion in the S/C range of 1.0-3.0 can be interpreted by a slow, but detectable take-off of SR that is coupled with POX. The explanations given above are in accordance with the literature information that states the higher chance of occurrence of POX in monolithic, straight channel type reactors characterized by narrow residence time distribution (RTD) and syngas production of by sequential occurrence of TOX (Eq.4.5) and SR in packed-bed structures known with wider RTDs (Onsan and Avci, 2011).

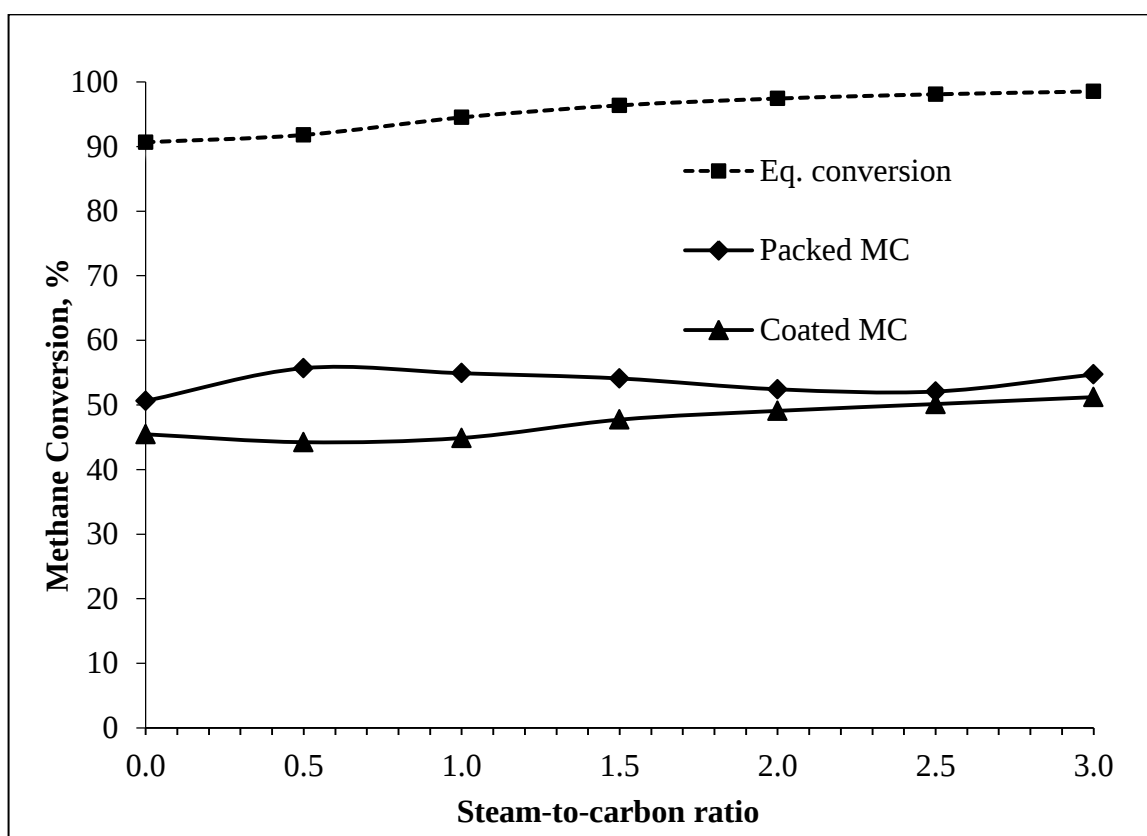


Figure 4.33. Effect of S/C ratio on CH₄ conversion over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels and on equilibrium conversions (inlet CH₄=14.3 mol%, O₂/C= 0.47, W_{cat}/F_{CH₄,0}= 0.356 mg·min·cm⁻³).

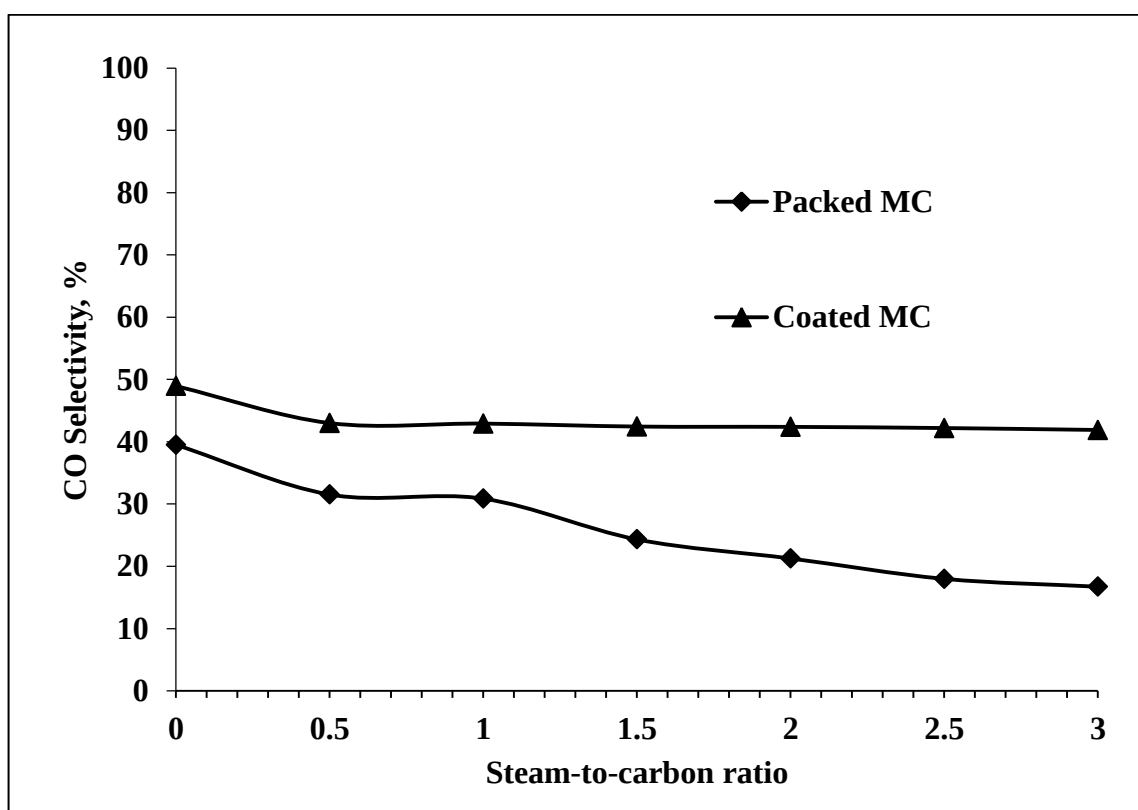


Figure 4.34. Effect of S/C ratio on CO selectivity over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels (inlet $\text{CH}_4 = 14.3 \text{ mol\%}$, $\text{O}_2/\text{C} = 0.47$, $W_{\text{cat}}/F_{\text{CH}_4,0} = 0.356 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$).

4.3.3. Effect of Inlet Oxygen-to-Carbon (O_2/C) Ratio

Figures 4.35-36 give the impact of oxygen-to-carbon ratio on methane conversion and CO selectivity obtained over coated and packed microchannels. In these experiments, O_2/C is varied between 0.47 and 0.63, while S/C ratio, reaction temperature and contact time are kept constant at 3.0, 923 K and $0.36 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$, respectively. Response of methane conversion against changes in the O_2/C ratio is found to be similar on both reactor geometries. Enriching the feed stream with oxygen improved the oxidation conversion of methane and led to the increasing shown in Figure 4.34. As observed in the previous results, the measured conversions are significantly below the theoretical equilibrium limit due to the operation at short residence times (ca. 12.9 ms).

Increasing the O_2/C ratios led to decrease in the CO selectivities delivered by both reactor configurations (Figure 4.35). The rate of decrease in the packed microchannel is found to be slightly higher than the coated one, especially in the O_2/C range of 0.47-0.54. As discussed in Section 4.3.2, the random-natured, wide-RTD flow distribution of the packed structure is likely to favor TOX (Equation 4.5) that produces CO_2 and H_2O . Due to the definition given in Equation 4.3, CO_2 production leads to reduction in the CO selectivity, which is also possible by the synthesis of extra H_2O that can shift the WGS in the direction of CO consumption. In contrast with the notable decrease in the O_2/C interval of 0.47-0.54, a nearly flat selectivity is observed in the 0.54-0.63 range. A possible explanation of this trend shift is by the take-off of reverse-WGS. Further enrichment of the feed with oxygen is known to improve TOX conversion to produce more CO_2 , part of which can then be converted back to CO to counter-balance the decreasing trend in selectivity. CO selectivities obtained in the coated microchannel seem to remain almost unaffected by the oxygen content in the feed, and are much higher than those measured in the packed microchannel. These finding can be supported by the previously stated argument of the possible POX mechanism that doesn't produce any CO_2 or H_2O . It is also worth noting that higher oxygen quantities fed can shift the oxidation stoichiometry from POX to TOX, hence lead to some CO_2 formation. This can provide an interpretation of the very slow decrease in the coated-channel CO selectivity shown in Figure 4.35.

The effect of O_2/C ratio on syngas composition is given in Table 4.6. As discussed above, the presence of TOX (Equation 4.5) stoichiometry, which leaves less methane for SR upon injection of more oxygen into the feed and reduces H_2 production, can explain the decreasing H_2/CO ratios obtained in the packed microchannel. However, the syngas composition seems to be almost unaffected by the quantity of oxygen fed, which is likely to be consumed by POX. The very small overall increase in the syngas ratio can be linked to the increased POX conversion that slightly favors H_2 production according to the stoichiometry dictated by Equation 4.4.

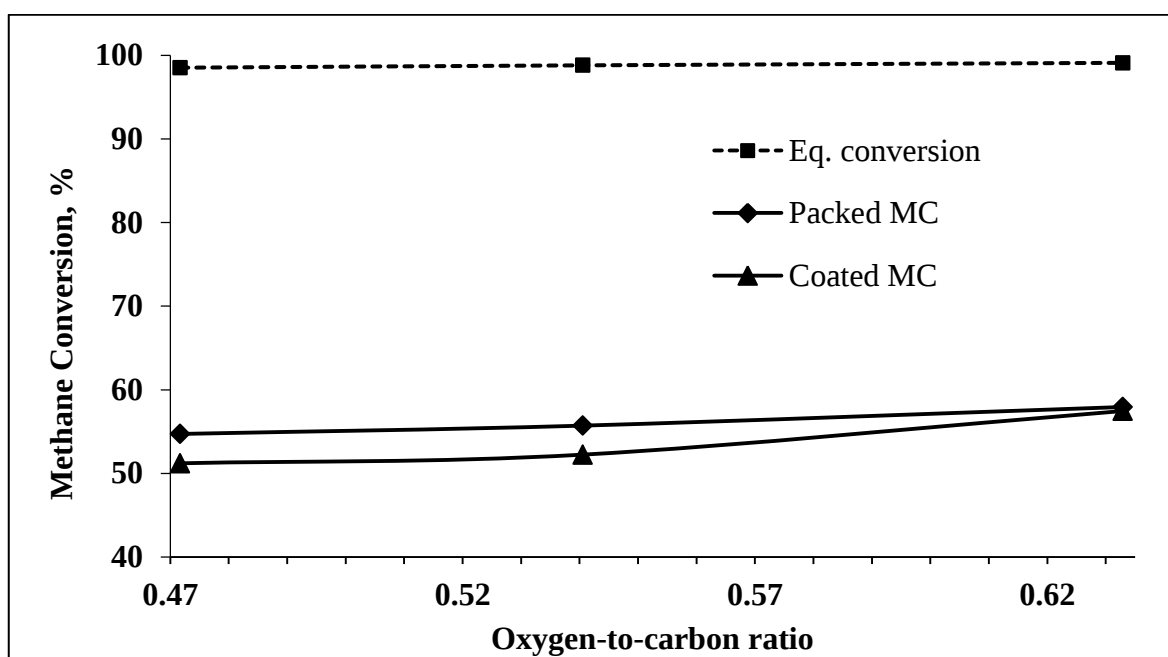


Figure 4.35. Effect of O_2/C ratio on methane conversions obtained over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels and on equilibrium conversions (inlet CH_4 = 14.3 mol%, S/C = 3.0, $W_{cat}/F_{CH_4,0}$ = 0.356 $mg \cdot min^{-1} \cdot cm^{-3}$).

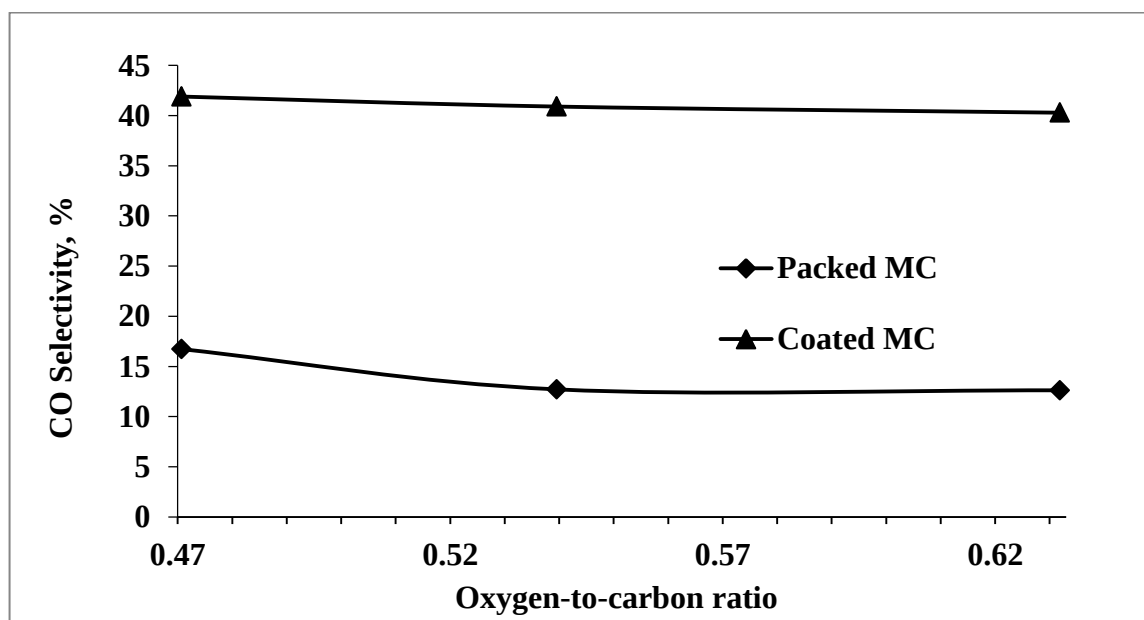


Figure 4.36. Effect of O_2/C ratio on CO selectivity over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels (inlet CH_4 = 14.3 mol%, S/C = 3.0, $W_{cat}/F_{CH_4,0}$ = 0.356 $mg \cdot min^{-1} \cdot cm^{-3}$).

4.3.4. Effect of Contact Time

Figures 4.37-38 show the effect of contact time on methane conversion and CO selectivity measured in the product spectra of coated and packed microchannel geometries. The experiments are conducted by varying contact time between 0.36-0.71 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$ while keeping reaction temperature, S/C and O_2/C constant at 923 K, 3.0 and 0.47, respectively. The expected increase in methane conversion with longer contact of the reactive stream with the catalyst bed is observed in both reactor types (Figure 4.37). As noted in the previous results, conversions remained well below the equilibrium limit, but did not deviate significantly from each other. Despite the notable gap between them, CO selectivities of both reactor configurations are found to respond similarly against increase in the contact time (Figure 4.38). The elevations observed in the 0.36-0.41 $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$ range are expected to be due to slightly pronounced impact of the expected CO-producing stoichiometries, namely SR and POX in the packed and coated microchannels, respectively. Further increase in the contact time, however, did not improve the CO selectivity. The possible root cause of this effect is TOX (Equation 4.5), which is known to be more effective at longer residence times to produce CO_2 sufficient to balance the increase in the CO selectivity. It is worth noting that the take-off of TOX can be observed better in the coated microchannel in which the elevation and flat zones in CO selectivity can be easily distinguished. On the other hand, the slower rate of increase of selectivity in the packed geometry is an indication of co-existence of CO-producing SR with CO_2 -producing TOX due to the wider RTD nature of the packed structure.

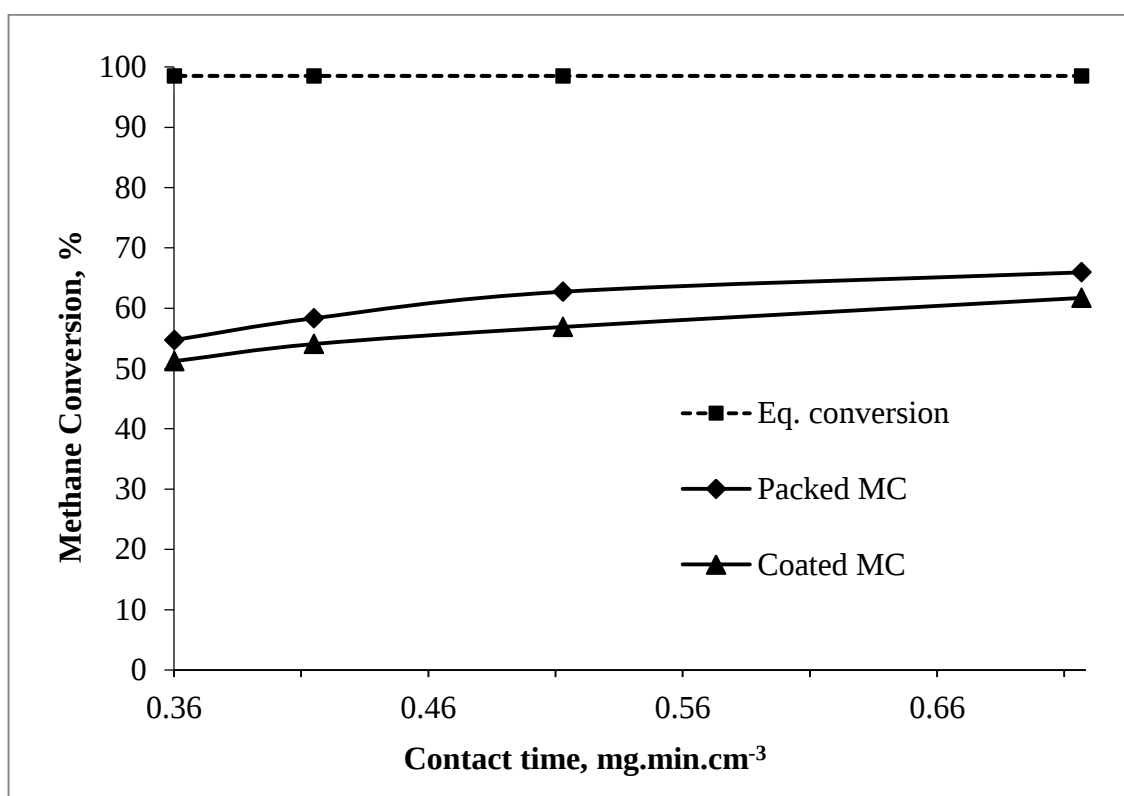


Figure 4.37. Effect of contact time on CH₄ conversion over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels and on equilibrium conversions (T= 923 K, inlet CH₄=14.3 mol%, S/C= 3.0, O₂/C= 0.47).

In addition to the trendwise similarities in their methane conversion and CO selectivities, H₂/CO ratios obtained in both catalyst geometries are found to respond similarly to change in the residence time (Table 4.6). However, as commonly observed from the previous outcomes, the coated geometry produced syngas ratios that at least three times less than those of the packed one.

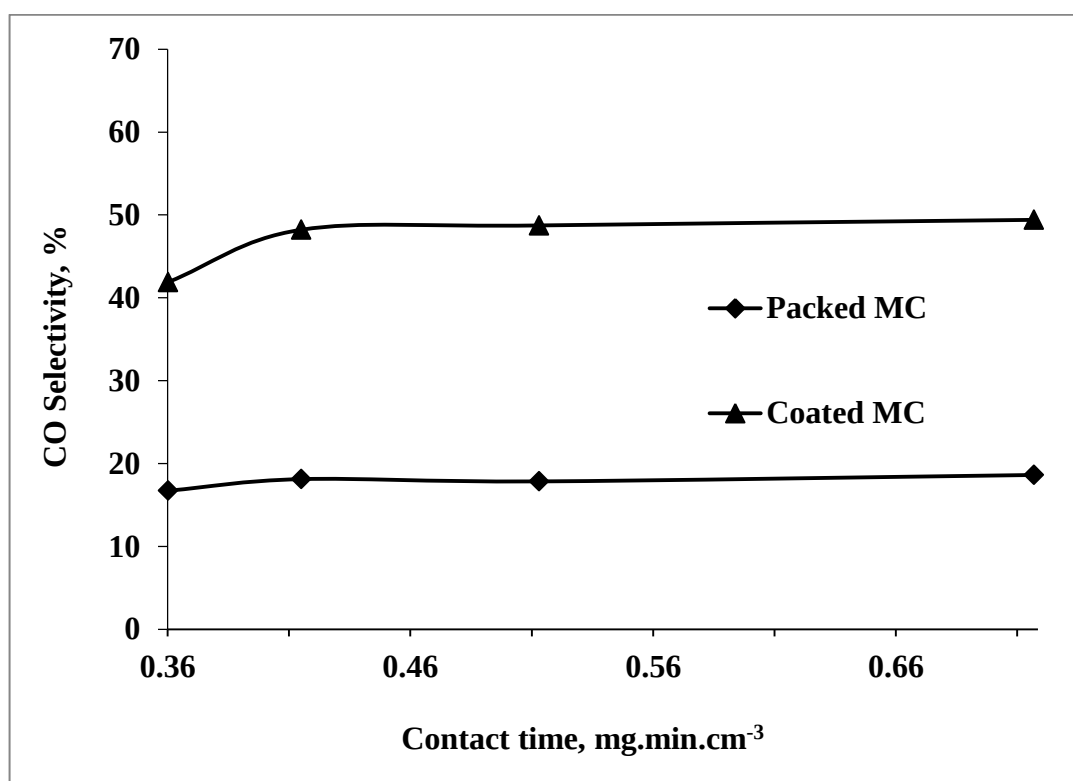


Figure 4.38. Effect of contact time on CO selectivity obtained over 0.2wt%Pt-2wt%Rh in packed and coated (Karakaya, 2012) microchannels and on equilibrium conversions ($T=923$ K, inlet $\text{CH}_4=14.3$ mol%, $\text{S/C}=3.0$, $\text{O}_2/\text{C}=0.47$).

4.4. OSR of Methane in Packed Microchannel Reactors over Monometallic Catalyst

The major aim of this part of the study is to investigate performance of monometallic 2wt%Rh and compare with bimetallic 0.2wt%Pt-2wt%Rh catalyst for syngas production in packed microchannel reactor geometries. OSRM experiments are carried out at 773, 823, 873 and 923 K and at atmospheric pressure with steam-to-carbon-ratios of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, and oxygen-to-carbon ratios of 0.0, 0.47, 0.54 and 0.63, using weight-based contact times of 0.35, 0.41, 0.50 and 0.71 $\text{mg} \cdot \text{min} \cdot \text{cm}^{-3}$.

4.4.1. Effect of Reaction Temperature

The effect of reaction temperature on methane conversion and CO selectivity obtained over coated and packed microchannel configurations are reported in Figures 4.39-40. The feed composition is kept constant at an inlet methane concentration of 14.3% (by

mole). S/C and O₂/C molar ratios of 3.0 and 0.47, respectively, and contact time of 0.36 mg·min·cm⁻³ are used in the experiments. It can be observed that, regardless of the 0.2%Pt addition to 2% Rh catalyst, methane conversion increased with temperature due to its positive effect on the reaction rates. The conversions are also similar quantitatively. Both catalysts delivered close values of methane conversions which are found to differ slightly (i.e. by ca. 5%) from each other.

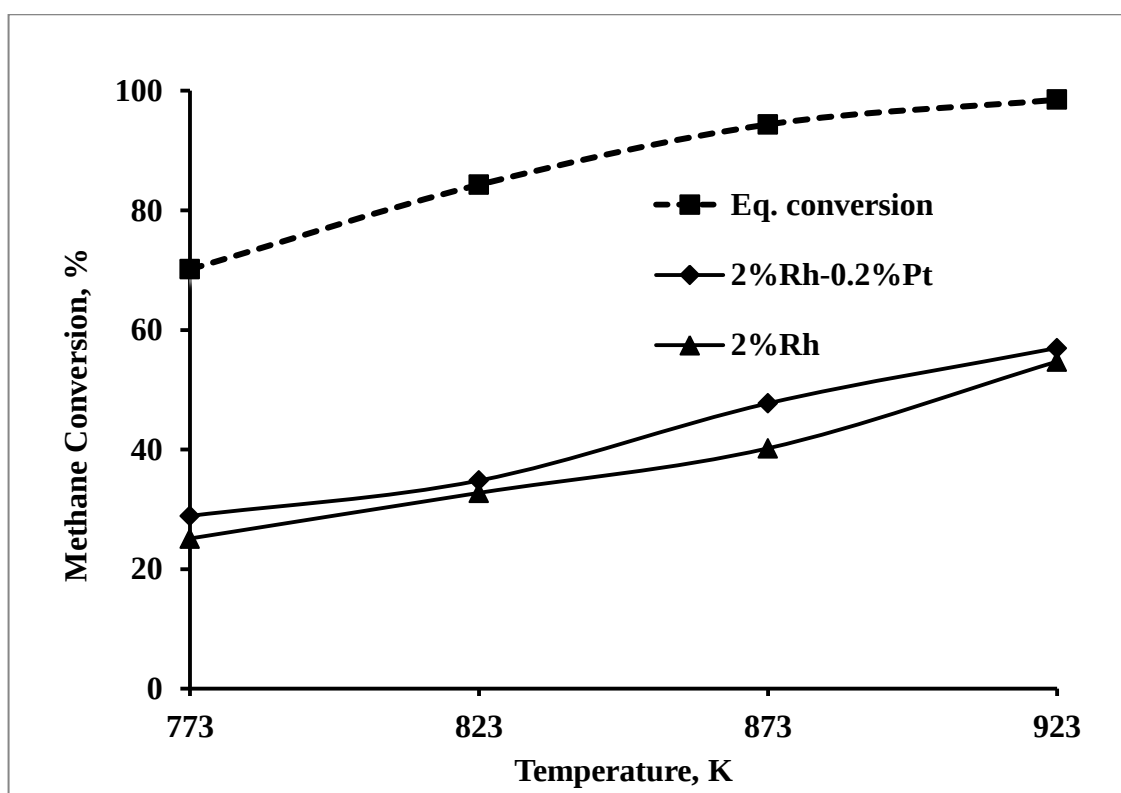


Figure 4.39. Effect of temperature on CH₄ conversion over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet CH₄=14.3 mol%, S/C= 3.0, O₂/C= 0.47, W_{cat}/F_{CH₄,0}= 0.356 mg·min·cm⁻³).

Full oxygen conversion is achieved in all runs, indicating that total oxidation is much faster than MSR and that increasing temperature only enhances the reforming conversion. The Pt active sites present on the catalyst surface catalyze total oxidation of methane, thus the generating energy necessary for the endothermic steam reforming reaction occurring on adjacent Rh sites (Çağlayan *et al.*, 2005).

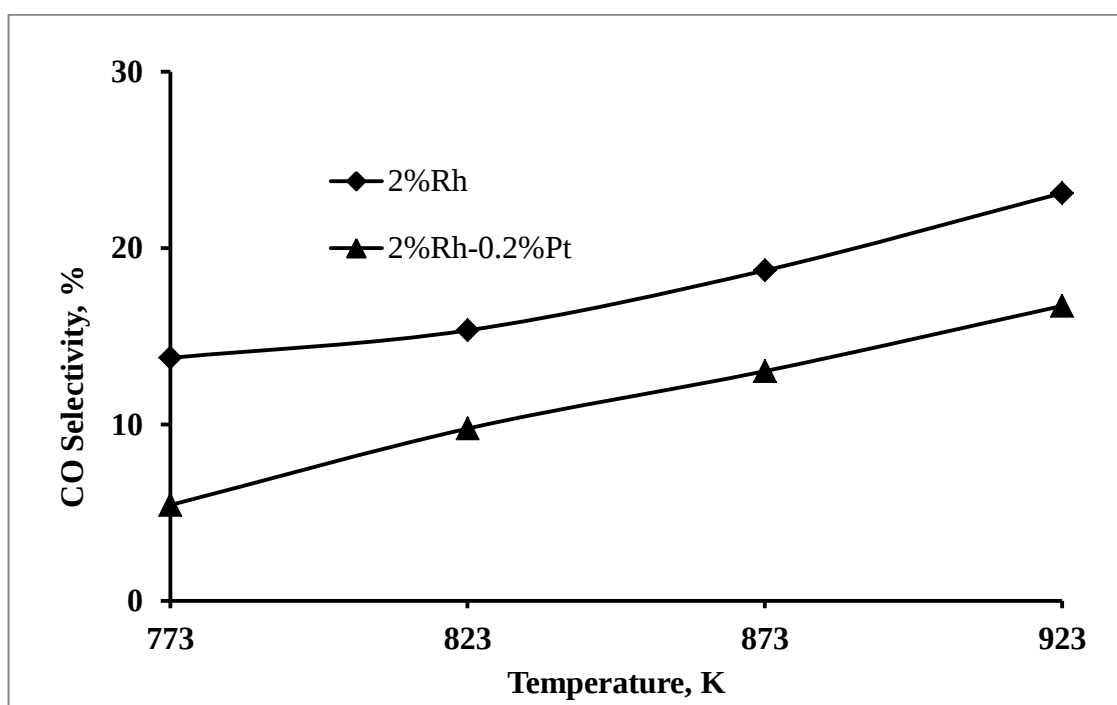


Figure 4.40. Effect of temperature on CO selectivity over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet CH_4 = 14.3 mol%, S/C = 3.0, O_2/C = 0.47, $W_{\text{cat}}/F_{\text{CH}_4,0}$ = $\text{mg} \cdot \text{min} \cdot \text{cm}^{-3}$).

For monometallic and bimetallic catalysts, CO selectivity increases to some extent. CO selectivity reached at 923 K is only 16.7 and 23.1, respectively over 0.2wt%Pt-2wt%Rh and 2wt%Rh catalysts. Comparing two catalysts, lower CO selectivity values are obtained over 0.2wt%Pt-2wt%Rh catalyst for whole temperature range because water gas shift activity seems to suppress the partial oxidation of methane.

4.4.2. Effect of Inlet Steam-to-Carbon Molar Ratio

The effect of steam-to-carbon ratio on methane conversion and CO selectivity obtained over 0.2wt%Pt-2wt%Rh and 0.2wt%Pt-2wt%Rh in packed microchannel configuration are shown in Figures 4.41-42. In these set of experiments, S/C is varied between 0 and 3.0, while O_2/C ratio, reaction temperature and contact time are kept constant at 0.47, 923 K and $0.36 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$, respectively. In contrast with temperature, the effect of steam addition on methane conversion is found to be minimal.

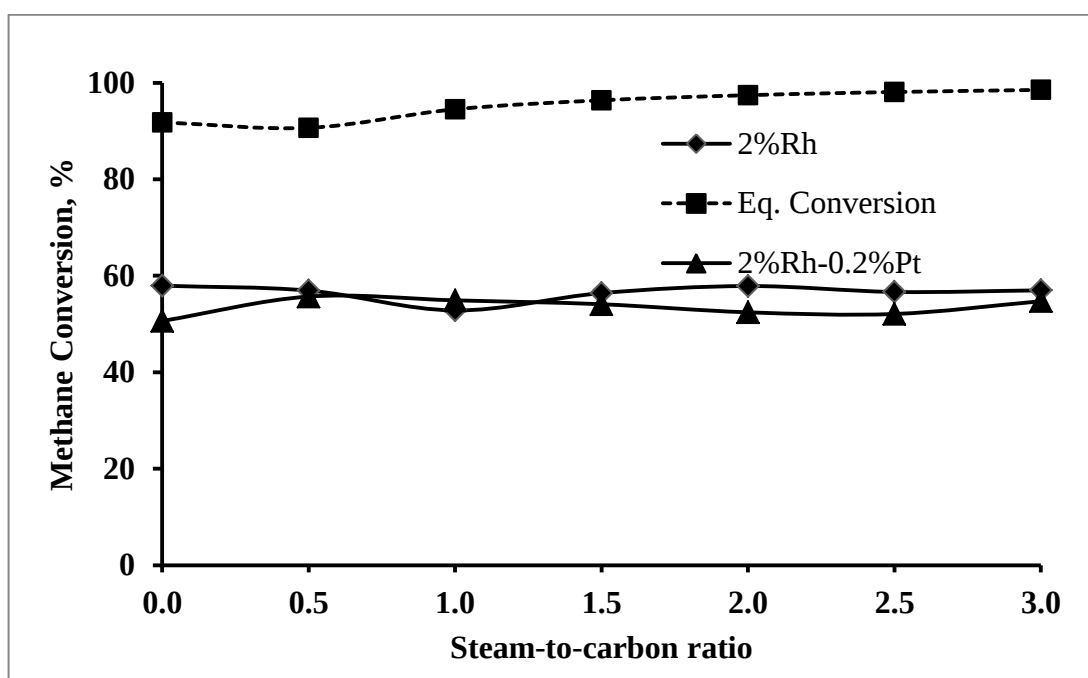


Figure 4.41. Effect of S/C ratio on CH_4 conversion over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet $\text{CH}_4 = 14.3 \text{ mol}\%$, $T = 923 \text{ K}$, $\text{O}_2/\text{C} = 0.47$, $W_{\text{cat}}/F_{\text{CH}_4,0} = 0.356 \text{ mg} \cdot \text{min} \cdot \text{cm}^{-3}$).

Although methane conversion levels reached on 2wt%Rh in packed microchannels are higher than those in coated microchannel reactors at most S/C molar ratios, there is not much difference and methane conversion is approximately at the level of 50 %. Moreover, increasing the S/C ratio does not promote methane conversion significantly, in contrast to the case of MSR presented in the former section (Section 4.2) in which methane conversion increases to some extent with increasing S/C molar ratio. Contribution of the steam concentration to methane conversion is suppressed most probably by oxygen addition producing water by total oxidation. When S/C is raised, CO selectivity is expected to decrease due to the fact that the reforming reaction is promoted by the higher reactant concentration (Figure 4.42). This is supported by experiments in which the S/C is increased from 0.0 to 3.0 (Figure 4.43), resulting in an increase in the product H_2/CO ratio from 2.88 to 8.53 over 0.2wt%Pt-2wt%Rh, and from 2.62 to 7.31 over 2wt%Rh. A noteworthy result is that H_2/CO ratios delivered by 0.2wt%Pt-2wt%Rh catalyst are higher those delivered by 0.2wt%Pt-2wt%Rh catalyst in packed microchannel configuration.

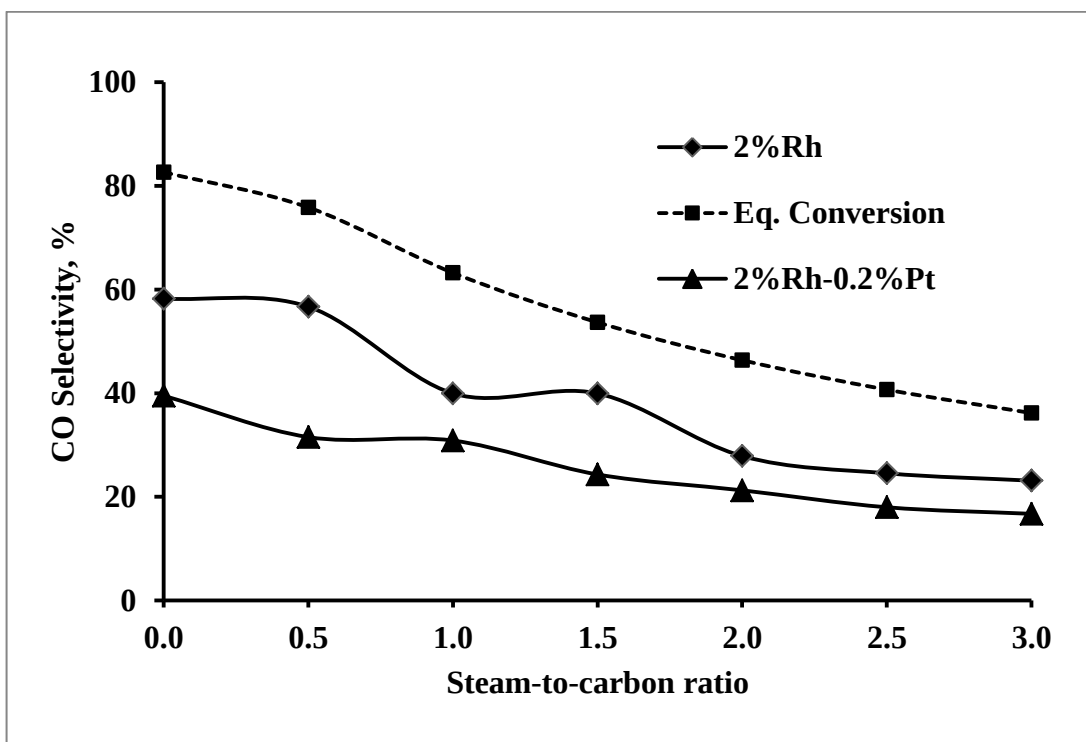


Figure 4.42. Effect of S/C ratio on CO selectivity over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet $\text{CH}_4=14.3$ mol%, $T=923$ K, $\text{O}_2/\text{C}=0.47$, $W_{\text{cat}}/F_{\text{CH}_4,0}=0.356$ $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$).

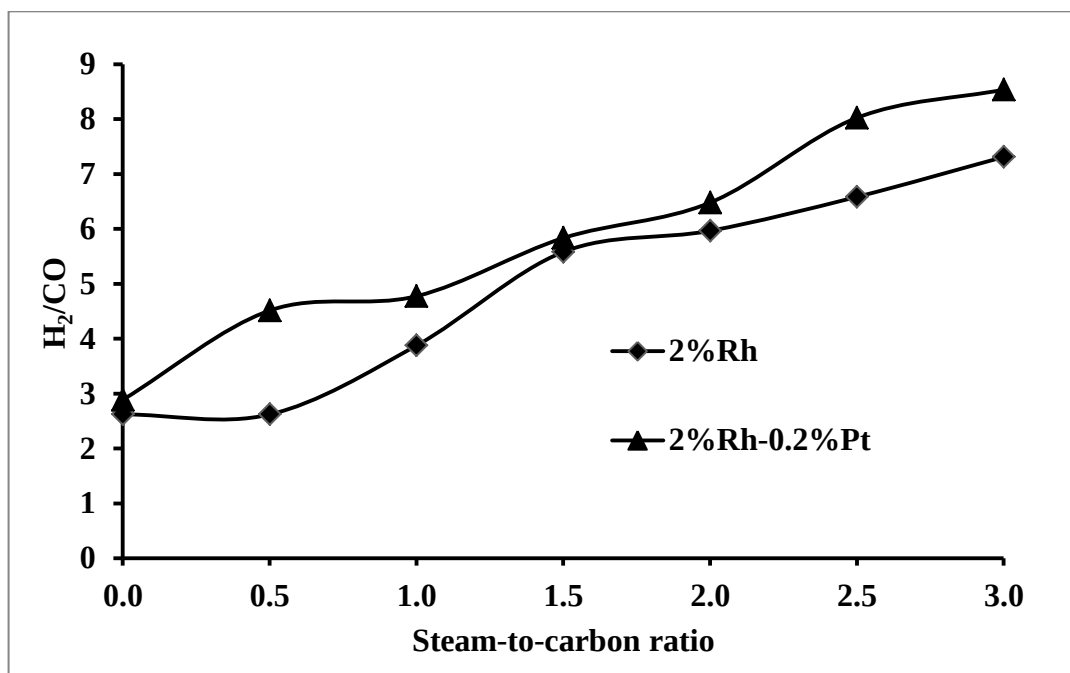


Figure 4.43. Effect of S/C ratio on H_2/CO ratio over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet $\text{CH}_4=14.3$ mol%, $T=923$ K, $\text{O}_2/\text{C}=0.47$, $W_{\text{cat}}/F_{\text{CH}_4,0}=0.356$ $\text{mg}\cdot\text{min}\cdot\text{cm}^{-3}$).

4.4.3. Effect of Inlet Oxygen-to-Carbon (O_2/C) Ratio

Figures 4.44-45 give the impact of oxygen-to-carbon ratio on methane conversion and CO selectivity obtained over 0.2wt%Pt-2wt%Rh and 2wt%Rh in packed microchannels. In these experiments, O_2/C is varied between 0.47 and 0.63, while S/C ratio, reaction temperature and contact time are kept constant at 3.0, 923 K and 0.36 $\text{mg} \cdot \text{min} \cdot \text{cm}^{-3}$, respectively. Response of methane conversion against changes in the O_2/C ratio is found to be similar on both reactor geometries. Enriching the feed stream with oxygen improved the oxidation conversion of methane and led to the increasing shown in Figure 4.44. As observed in the previous results, the measured conversions are significantly below the theoretical equilibrium limit due to the operation at short residence times (ca. 12.9 ms).

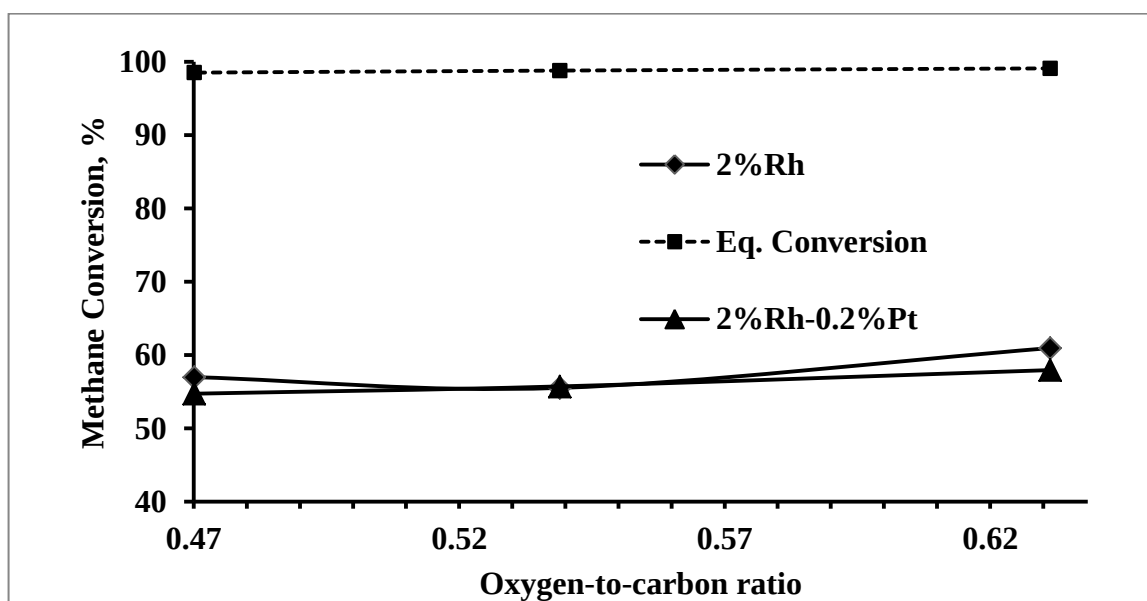


Figure 4.44. Effect of O_2/C ratio on CH_4 conversion over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet CH_4 = 14.3 mol%, T = 923 K, S/C = 3, $W_{cat}/F_{CH_4,0}$ = 0.356 $\text{mg} \cdot \text{min} \cdot \text{cm}^{-3}$).

As for the effect of O_2/C ratio, total oxidation conversion increases with increasing oxygen partial pressure, and the amount of extra water produced increases steam reforming conversion to a limited extent. Although the CO selectivity over 0.2wt%Pt-2wt%Rh catalyst decreases slightly, the CO selectivity over 2wt%Rh does not vary with increasing oxygen partial pressure in the feed stream. This behavior is expected for the low O_2/C

values, since the heat supplied by oxidative reforming of methane over Pt sites compensates for the heat requirement of methane reforming, and consequently more hydrogen is produced over 0.2wt%Pt-2wt%Rh.

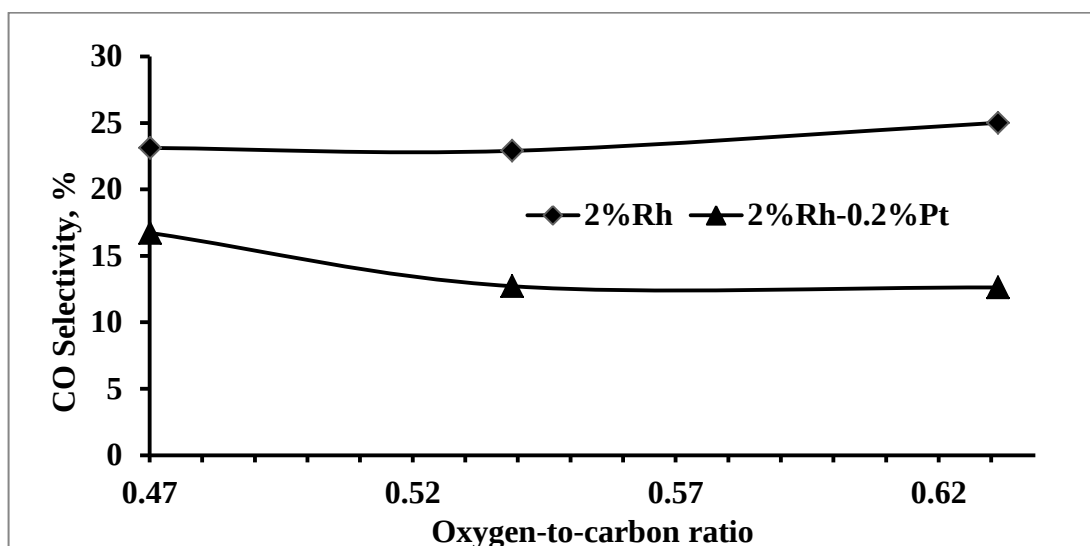


Figure 4.45. Effect of O_2/C ratio on CO selectivity over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet $CH_4 = 14.3$ mol%, $T = 923$ K, $S/C = 3$, $W_{cat}/F_{CH_4,0} = 0.356$ mg·min·cm⁻³).

4.4.4. Effect of Contact Time

Figures 4.46-47 show the effect of contact time on methane conversion and CO selectivity over 0.2wt%Pt-2wt%Rh and 2wt%Rh catalysts in packed microchannels. The experiments are conducted by varying contact time between 0.36-0.71 mg·min·cm⁻³ while keeping reaction temperature, S/C and O_2/C constant at 923 K, 3.0 and 0.47, respectively.

As contact time is increased from 0.36 to 0.71 mg·min·cm⁻³, the methane conversion over 0.2wt%Pt-2wt%Rh increases from 54.7 to 65.9% while that over 2wt%Rh in packed microchannel increases from 56.9 to 71.3% in a similar manner. It is drawn from these results, 0.2%Pt has almost no effect on methane conversion with contact time variation. Near the reactor walls, the packing density is lower than the mean value, and faster flow of the fluid near the wall is unavoidable. The catalyst particles might be bypassed by the reactant and residence time distribution will be broadened. The OSRM performance measured in terms of methane conversion obtained in contact time experiments clearly

indicates that using a packed microchannel reactor may indeed eliminate the issues mentioned for the conventional packed bed reactor (Renken and Minsker, 2010). This improvement suppressed the influence of contact time increase on methane conversion and CO selectivity.

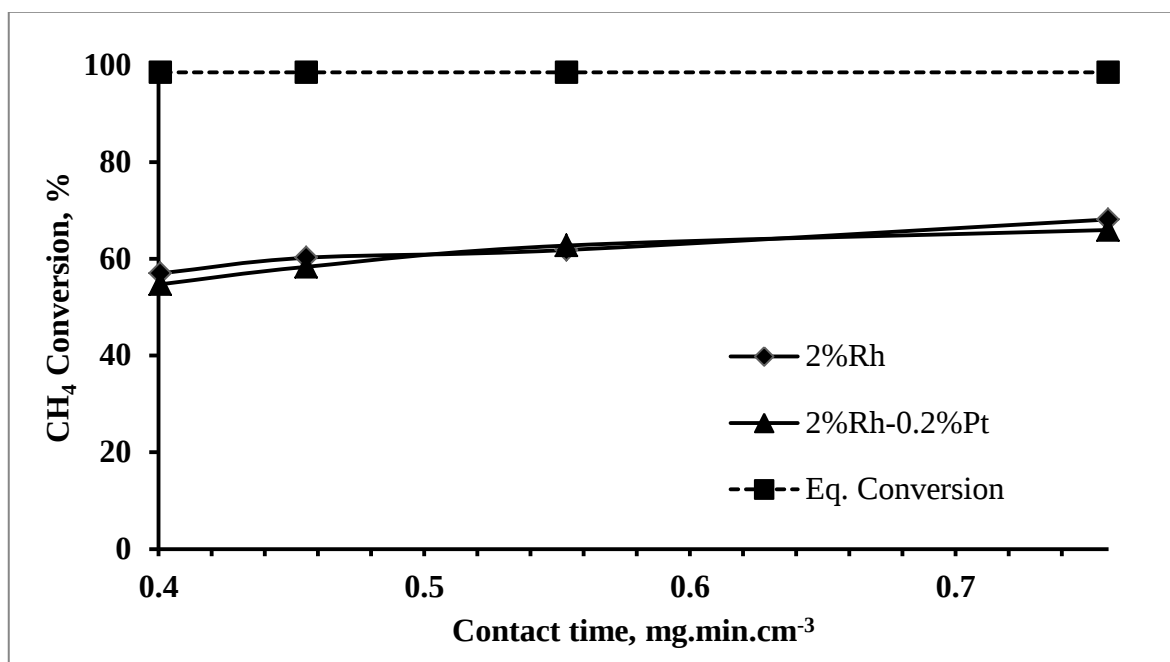


Figure 4.46. Effect of contact time on CH₄ conversion over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet CH₄= 14.3 mol%, T= 923 K, S/C= 3, O₂/C= 0.47).

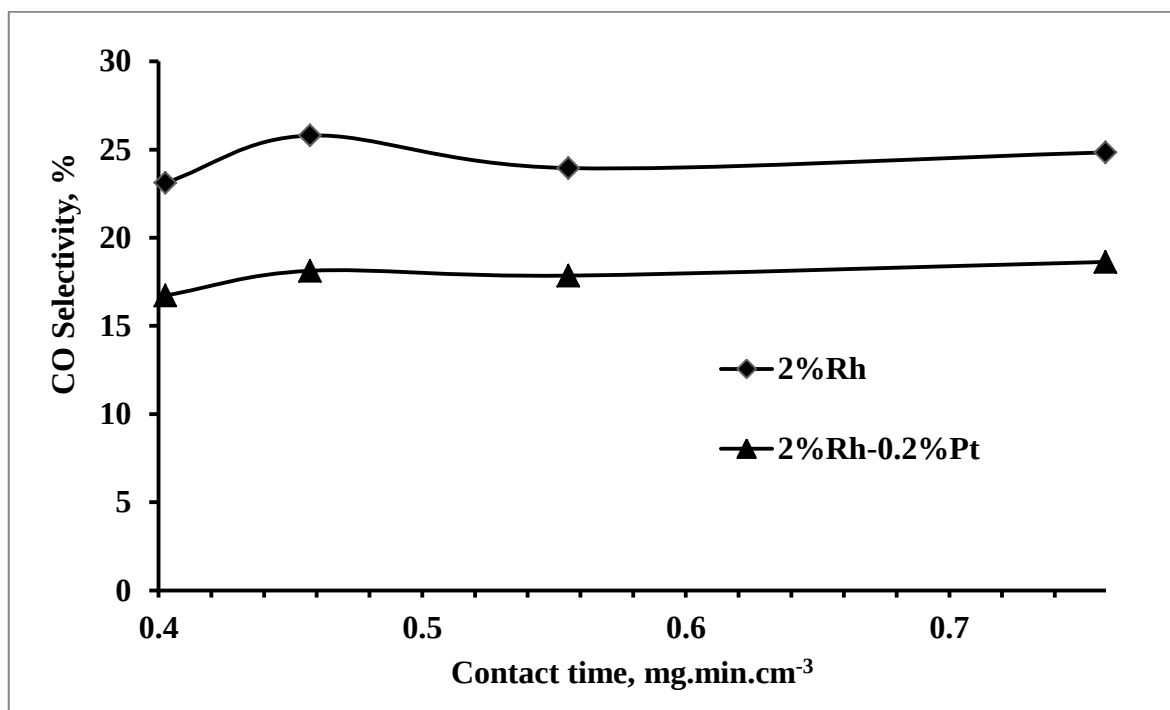


Figure 4.47. Effect of contact time on CO selectivity over 0.2wt%Pt-2wt%Rh and 2wt%Rh (inlet CH₄=14.3 mol%, T= 923 K, S/C= 3, O₂/C= 0.47).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

This dissertation presents syngas production from methane by steam and oxidative steam reforming (MSR and OSRM) in novel design wall-coated and packed microchannel reactors over δ -Al₂O₃ supported Ni and precious metal (Rh, Ru, Pd, Pt) based catalysts. The work conducted consists of three distinct parts: (a) MSR in conventional packed bed microreactors over δ -Al₂O₃ supported Ni, Pt-Ni, Pd, Rh and Ru; (b) comparison of the MSR performances of δ -Al₂O₃ supported 2wt% Rh, 2wt% Ru and 2wt% Pd together with 10wt% Ni for syngas production in two different microchannel reactor geometries, namely packed and wall-coated microchannels; (c) OSRM in a packed single microchannel reactor having two uncoated plates with δ -Al₂O₃ supported 0.2wt%Pt-2wt%Rh bimetallic catalyst packing in between and its comparison with data obtained by Karakaya (2012) in the wall-coated microchannel reactor configuration, as well as comparison of the performances of δ -Al₂O₃ supported 0.2wt%Pt-2wt%Rh bimetallic and monometallic 2wt%Rh particulate catalysts in the packed single microchannel configuration.

(i) The following conclusions can be drawn on the basis of the work conducted in the conventional packed-bed microreactor for assessing MSR activities of Ni/ δ -Al₂O₃, Pt-Ni/ δ -Al₂O₃, Pd/ δ -Al₂O₃, Rh/ δ -Al₂O₃ and Ru/ δ -Al₂O₃: Ni sites (i) almost cover the δ -Al₂O₃ surface, and (ii) are dispersed homogenously. In addition, as indicated by EDX analysis, the impregnated Ni content in catalyst is 14.84% in parallel with the targeted amount of 15%.

- Methane conversion decreases with increasing catalyst particle size indicating the existence of internal mass transport resistances in larger particles. In order to eliminate internal transport resistances, catalytic activity tests are conducted with average particle size 300 μ m.
- Rh-based catalyst is distinguished from others in that it is quite not affected by temperature changes in the 873-1023 K range and exhibits higher CH₄ conversions even at the lower temperatures.

- At the highest temperature tested, 1023 K, all catalysts exhibit similar conversions close to the equilibrium conversion level.
- Both methane conversions and product H_2/CO ratios are found to increase with increasing S/C molar ratio in the feed.
- In the presence of 10% CO_2 in the feed, methane conversion increases with temperature over all catalysts tested; the highest CH_4 conversion reached is 99% over Ni and Rh based catalysts at 1023 K.
- Unlike the other catalysts, methane conversions over $Pd/\delta-Al_2O_3$ and $Rh/\delta-Al_2O_3$ catalysts are not affected by the CO_2 addition due to lower WGS and methanation activity of these catalysts

(ii) The aim of second part of the study was to investigate and compare the MSR performances of $\delta-Al_2O_3$ supported precious metal and nickel catalysts (2wt% Rh, 2wt% Ru, 2wt% Pd, and 10wt% Ni) for syngas production in two different microchannel reactor geometries, namely wall-coated and packed microchannels, operated at 873-1023 K and S/C ratios of 2.5-3.5, using a fixed inlet methane concentration and identical contact times. The major conclusions that can be drawn from this part of the study are as follows:

- Methane conversions and consumption rates, and H_2 and CO production rates, reached in wall-coated microchannels are much higher than those in packed microchannels under the reaction conditions covered for all the catalysts tested. Wall-coated reactor configurations minimize transport resistances and provide uniform temperature distribution in the catalyst layer.
- In both configurations, H_2 and CO production rates over 2wt% Rh are the highest. H_2/CO molar ratios in wall-coated microchannel product streams are significantly lower than those in packed microchannels. 2wt% Rh is better in terms of CO selectivity while 10wt% Ni gives the highest H_2 selectivity.

These results indicate the possibility of reducing the H_2/CO ratio obtained in MSR by using wall-coated microchannel reformers for generating syngas suitable for gas-to-liquid applications.

(iii) In the third part of the study, OSRM performance of $\delta-Al_2O_3$ supported bimetallic 0.2wt%Pt-2wt%Rh catalyst was investigated in packed microchannel reactors by a parametric study involving variations in reaction temperature, contact time, and ratio of steam-to-carbon and oxygen-to-carbon is performed in the relatively lower temperature range of 773-923 K, and lower contact time region of 0.35 to 0.71 $mg \cdot min \cdot cm^{-3}$, using S/C ratios in the 0-3.0 range and O_2/C ratios between 0.47 and 0.62. The results obtained were compared with those obtained in wall-coated microchannel reactors by Karakaya (2012) as well as with those of the monometallic 2wt%Rh catalyst in the packed single microchannel configuration. The major conclusions that can be drawn from this part of the study are as follows:

- Increase in all of the parameter values led to improvement in methane conversion, while CO selectivity increased only with temperature and contact time.
- In all cases, methane conversions in both microchannel configurations are found to be comparable with each other, but notably below the thermodynamic limit due to the short contact times (~ 12.9 ms) employed
- CO selectivity, a critical parameter in syngas production, is found to be significantly higher in the coated microchannel configuration. On the other hand, packed microchannel reactor is characterized by the delivery of H_2 -rich syngas.
- The results provide some indications of the dependence of syngas production and water-gas shift mechanisms on different flow distribution characteristics of coated and packed microchannels.
- For all parameters, monometallic 2%Rh gives higher CO selectivity than bimetallic 0.2%Pt-2%Rh, and is therefore preferable for syngas production from CH_4 .

5.2. Recommendations

According to the results of the present study, the following points are thought to be beneficial for the future studies:

- Kinetic studies can be conducted on MSR over 2%Rh/ δ -Al₂O₃ catalysts which is the most promising catalyst in both microchannel reactors.
- Microchannel reactor design can be improved in order to be closer to a commercial design.
- Effect of the addition of CO₂ into the feed for MSR can be investigated in microchannel reactor configurations.
- Considering that 2%Rh/ δ -Al₂O₃ and 15%Ni/ δ -Al₂O₃ catalysts are promising for the MSR reaction, a bimetallic Rh-Ni catalyst can be prepared and tested for activity and selectivity in microchannel reactor configurations.

APPENDIX A: CALIBRATION CURVES OF MASS FLOW CONTROLLERS

The calibration curves of N₂, CH₄, H₂, CO₂ and dry air gases on mass flow controllers (MFCs) are shown in Figures A.1-5, respectively.

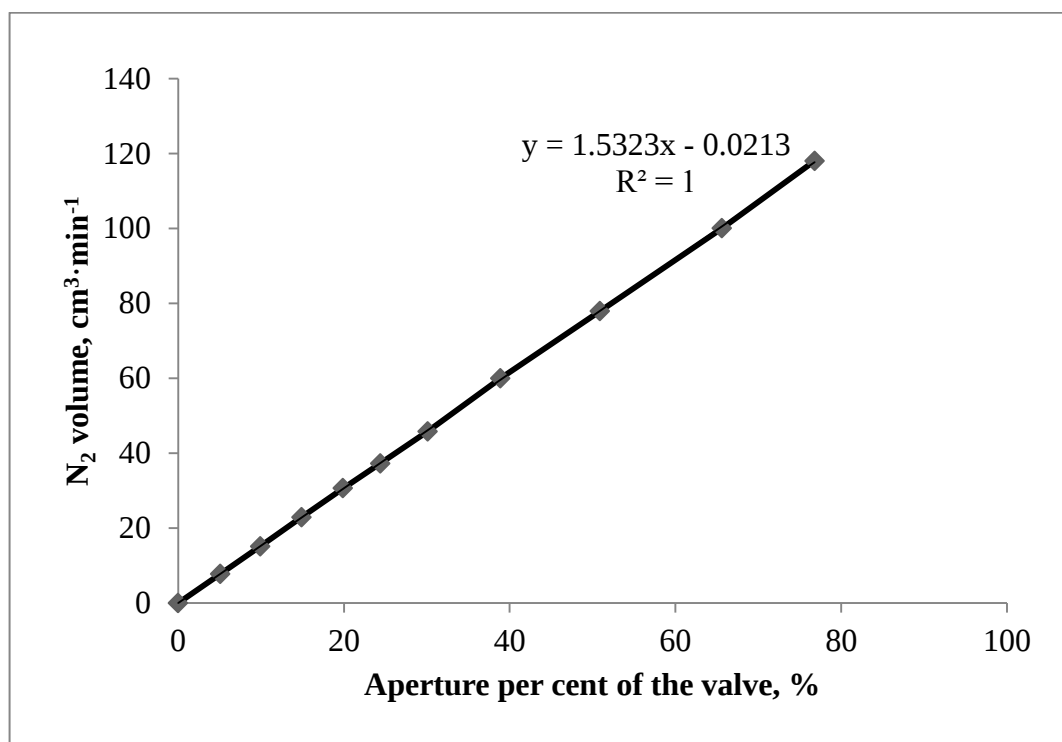
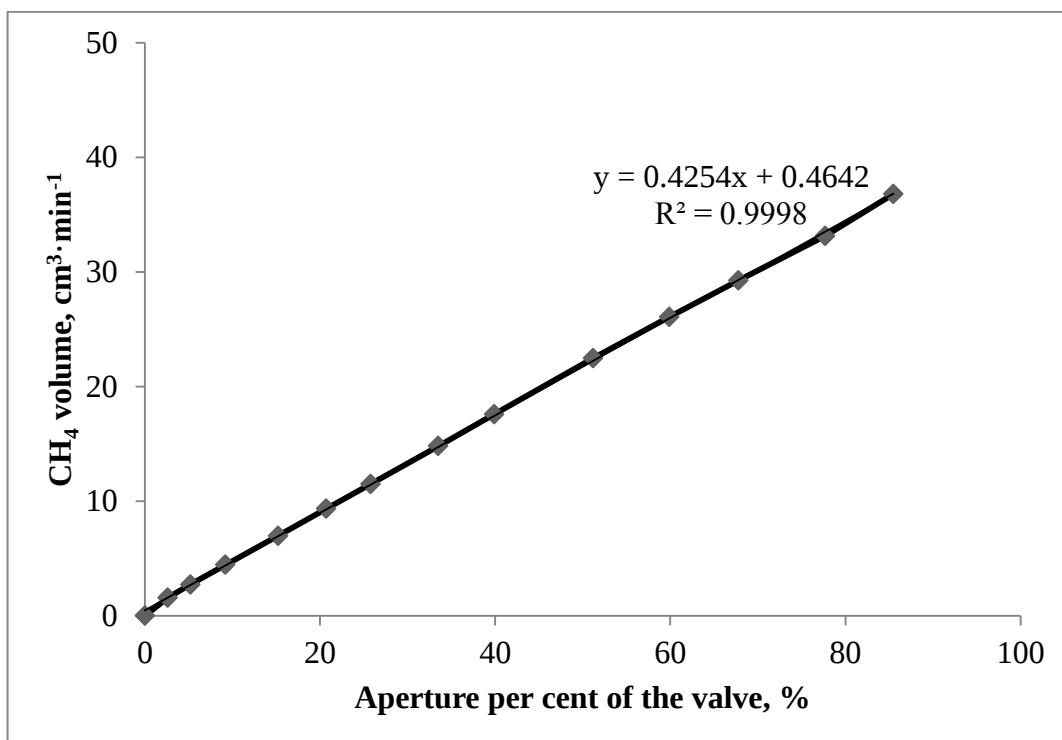
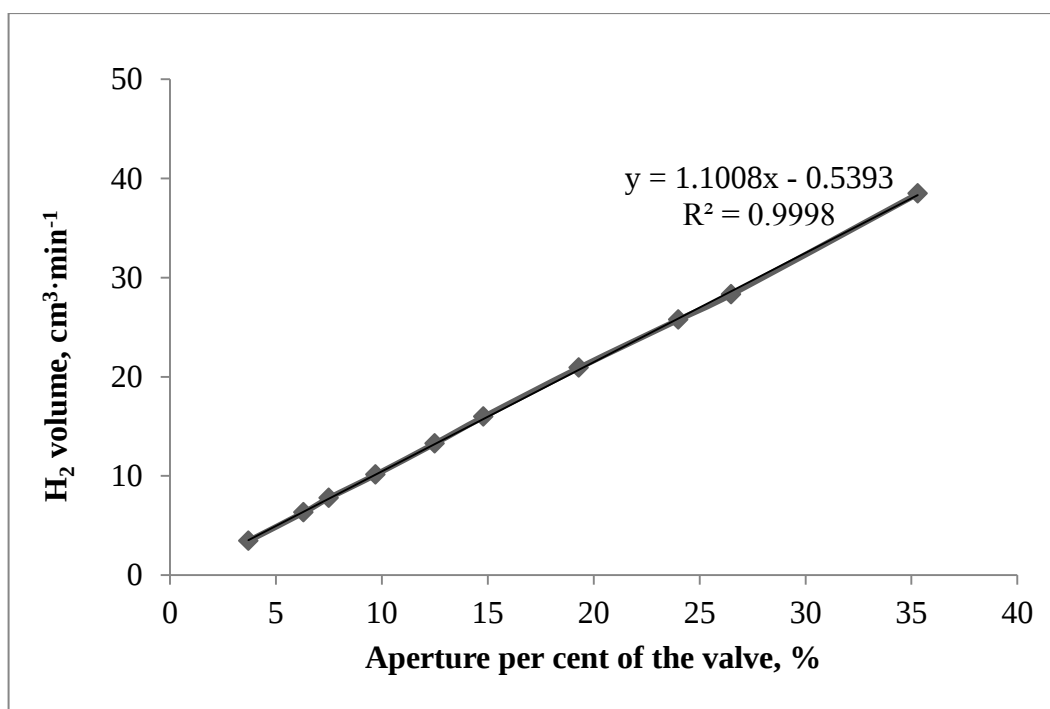


Figure A. 1. MFC calibration curve for N₂.

Figure A. 2. MFC calibration curve for CH₄.Figure A. 3. MFC calibration curve for H₂.

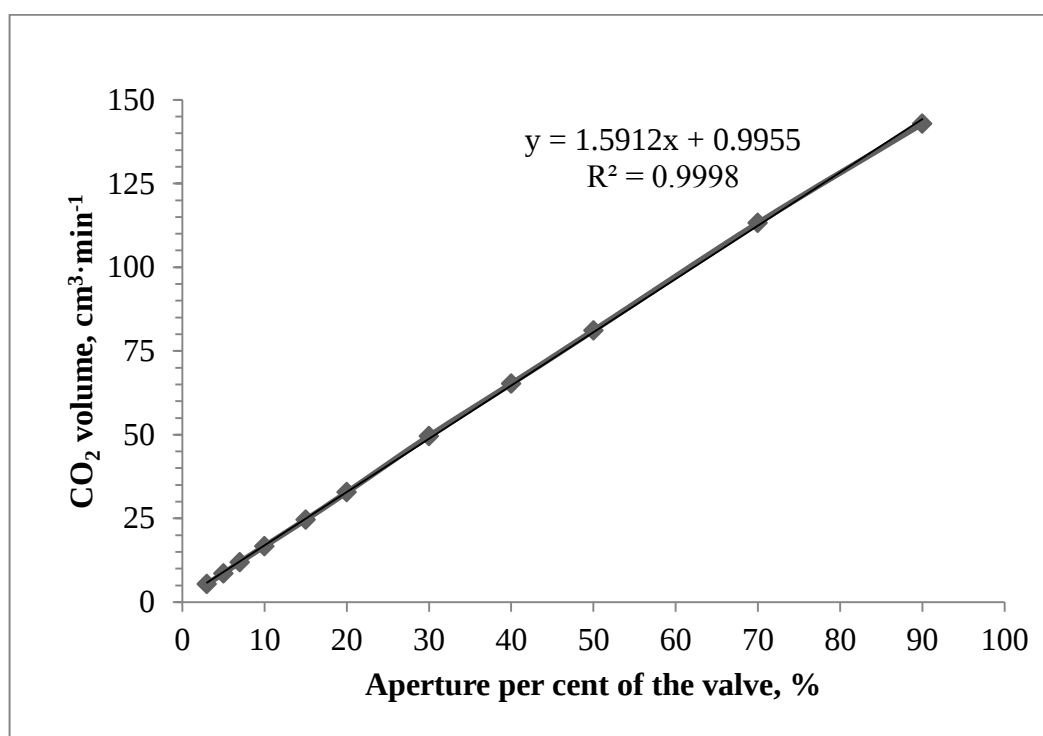
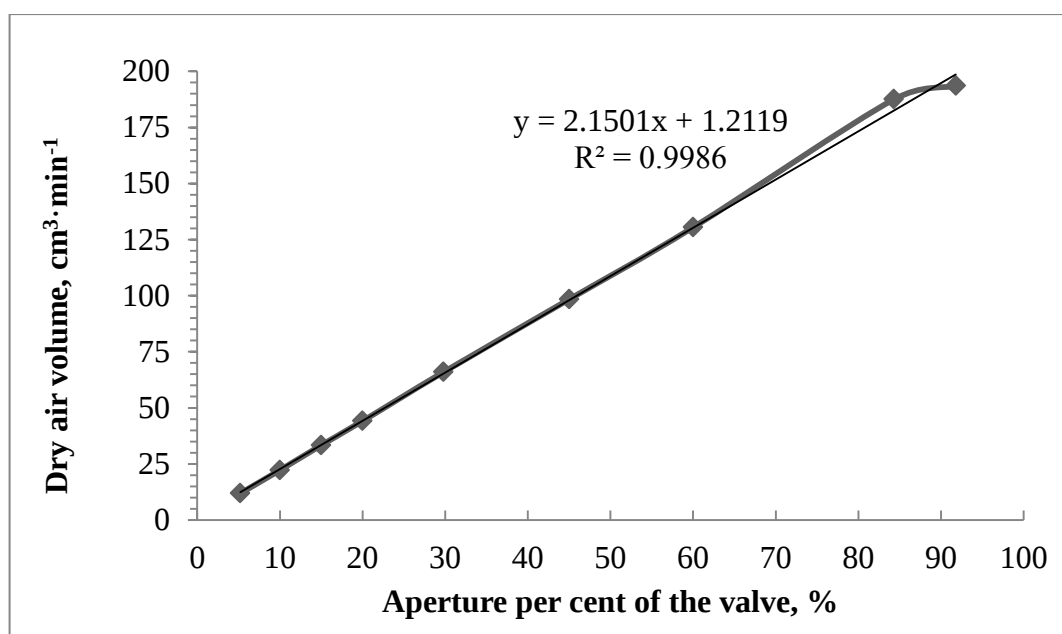
Figure A. 4. MFC calibration curve for CO₂.

Figure A. 5. MFC calibration curve for dry air.

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