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PRODUCTION OF CO/H2 MIXTURES FROM C1-C3 HYDROCARBONS OVER HONEYCOMB MONOLITHS

 Relatori:
 Prof.ssa Alessandra BERETTA

 Prof. Dr. Olaf DEUTSCHMANN

 (Institut für Technische Chemie und Polymerchemie-Universität Karlsruhe (TH))

 Tutor:
 Dipl. -Chem. Benjamin SCHÄDEL

Tesi di Laurea di:

Paolo PIERMARTINI Matr.667847

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1. Introduction and motivation:

1.1 Routes to Syngas and Hydrogen:

The energy policy is directed by the need for secure energy supply and by the wish for sustainable growth. This deals with efforts to decrease the dependency on oil in view of the limited resources and to increase the use of other *energy sources* than fossil fuels [1].

With the variety of energy sources, there is need for *energy carriers* to make easy transformations in the applications for power and automotive applications.

Catalytic process technology plays an increasing role in creating flexibility, by providing new routes and by development of environmental solutions for flue gas and exhaust gas cleaning.

One of these new energetic routes is the production of synthesis gas.

Synthesis gas is a mixture of hydrogen, carbon monoxide and carbon dioxide used in a number of highly selective syntheses of chemicals and fuels [2] and an important source of pure hydrogen and carbon monoxide.

Today, natural gas and other hydrocarbons are the dominant feedstock for the production of synthesis gas. The well-known synfuel cycle is here plotted:



Figure 1.1: The synfuel cycle [2]: ATR, autothermal reforming (1); Fischer-Tropsch synthesis (2); TIGAS, Topsøe integrated gasoline synthesis (4); MTG, Mobil methanol to gasoline process (5); DME, dimethyl ether (6); methanation for SNG (substitute natural gas) (7).

During the second world war benzine was produced out of this gas mixture using the process of Fischer-Tropsch ($nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$). In the 1970s there was another peak of the research about synthetic fuels because of the oil crisis. A technical advantage of the expensive synthetic fuels produced by Fischer-Tropsch is the fact, that they don't contain sulphur at all and that they have high octane numbers [2, 3].

Today coal in the field of producing synthesis gas (except in South Africa and Australia) has been replaced with natural gas, for reasons of economy [4]. Production of synthesis gas itself is highly efficient, but requires a very capital intensive equipment, so that e.g. 60% of the investment cost of industrial equipment made for production of natural gas are allotted to the production of synthesis gas.

However, equipment made for coal gasification costs three times as much as equipment for hydrocarbons [2, 5].

Each fuel containing carbon (coal, petroleum, natural gas and even biomass) can actually be used for the production of synthesis gas. Synthesis gas out of methane is considered as being environmentally friendly because of its potential application for fuel cells and because of the low production of CO_2 in consequence of the high ratio of hydrogen to carbon. It is relatively cheap because during oil production methane is obtained as a waste product, which is still burned at the moment.

Today synthesis gas is still a key intermediate within the basic material chemistry (Fischer-Tropsch, production of ammonia according to the process of Haber-Bosch, synthesis of methanol $CO + 2 H_2 \rightarrow CH_3OH$, production of pure hydrogen $CO + H_2O \rightarrow CO_2 + H_2$,...).

The present trends in the use of syngas are anyway strongly dominated by the conversion of inexpensive remote natural gas into liquid fuels ("gas to liquid"), and by a possible role in a hydrogen economy [2], as said above, with a consequent increasing demand of syngas.

Hence research over different hydrocarbon feedstock (normally ranged from natural gas to diesel), or works based on fundamental understanding of parameters influencing the catalyst specific activity, as well studies over catalyst with well-defined surface are basic [5].

Improvements in the practical efficiencies have been achieved over the years by a combination of chemical engineering and catalyst development [2].

Steam reforming of hydrocarbons is the preferred process for hydrogen and "syngas" (**syn**thesis **gas**) today [2].

It's a very well established technology; however, many issues are still open:

- For example in the methane steam reforming, yields are far from being economical, mostly depending on the high methane molecule stability (C-H bond energy of 439 kJ/mol) and the following resistance to different reactants.
- Even if synthesis gas routes are highly efficient, they are capital intensive too, in relation with the involved exchange of energy with reformers and heat-recovery units [2].
- The thermodynamics analysis shows how the conversion of methane is restricted by the reforming reaction. The endothermic steam reforming reactions must be carried out at high temperature and low pressure to achieve maximum conversion.
- The development of short contact time processes and reactors, generally based on the use of highly active noble-metal based catalysts, with structured configuration.
- The possibility to couple, through the co-feed of an oxidizing agent, exothermic and endothermic reactions with a positive impact on the energetic efficiency.

Considering the information presented in previous works [2, 3, 5-7], this research, employed in a larger study about chemical reaction mechanisms for heterogeneous catalysis, wants to establish an experimental data bank, for the development of kinetic schemes of hydrocarbons activation.

For this reason, the efficiency in conversion and products selectivity by steam reforming (**SR**) (both homogeneous and heterogeneous reaction), catalytic partial oxidation (**CPO**) and autothermal reforming (**ATR**) of light hydrocarbons, namely methane, ethane and propane, is here studied.

1.2 Production of hydrogen:

Hydrogen as an "energy vector" was discussed in the wake of the energy crisis in the 1970s. Today, "hydrogen economy" is high on the political agenda and on the priorities of agencies funding research. Hydrogen is claimed to replace hydrocarbons and to provide a clean fuel with no carbon emissions for use in stationary and mobile applications as well. Fuel cells, for example, will play a key role for both situations.

As said above, in the context of this thesis, the hydrogen providing processes like steam reforming, autothermal reforming (ATR) and catalytic partial oxidation (CPO) of light hydrocarbons, are examined:

Steam reforming:

$$C_nH_m + n H_2O \rightarrow n CO + (n + m/2) H_2 \qquad \Delta H^{\circ}_{298} > 0 (kJ/mol)$$
 (1.2)

 $CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ (kJ/mol)}$ (1.3)

Partial oxidation:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$
 $\Delta H^{\circ}_{298} = -38 \text{ (kJ/mol)}$ (1.4)

Autothermal reforming:

 $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ $\Delta H^{\circ}_{298} = -38 \text{ (kJ/mol)}$ (1.5)

$$CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$$
 $\Delta H^{\circ}_{298} = -803 \text{ (kJ/mol)}$ (1.6)

 $CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H^{\circ}_{298} = 206 \text{ (kJ/mol)}$ (1.7)

 $CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41 \text{ (kJ/mol)} \qquad (1.8)$

Steam reforming of methane is a highly endothermic reaction, as described above; therefore, external heating is normally required.

On the other hand, internal heat supplies are well known to be more energy efficient than external heat supply system. A well-known internal heat supplying system for syngas production is the autothermal reforming process (Eqs 1.5-1.8).

The autothermal reforming process is an hybrid of partial oxidation and steam reforming, using steam and oxygen. In this way, there is no need for external heat and that allows a decrease in the maximum temperature [2]. The hybrid solution, using a partial combustion in a flame followed by catalytic reaction, was pioneered by SBA and BASF in the 1930s [5].

In the ATR process, oxygen is fed together with methane and steam. The added oxygen engenders exothermic reactions, such as non-catalytic partial oxidation (Eq. 1.5) and combustion of methane (Eq. 1.6) in the non catalytic reaction zone. This heat is then used for the catalytic reforming reaction [8, 9].

These routes, shown before, provide hydrogen in a mixture with carbon monoxide, the socalled "syngas", as said.

The commercial techniques for obtaining a stream of pure hydrogen from the produced syngas, consist of one or two WGS-stages, and some purification stages.

In order to obtain a fuel-cell grade hydrogen, any trace of carbon monoxide has to be removed and a "CO-prox." (carbon monoxide preferential oxidation) catalytic stage provides the necessary requirements.

Anyway, in principle, any technique for producing syngas is a technique for the production of hydrogen.

Few techniques, however, have proper characteristics for integration with fuel cells, both stationary and mobile.

The conversion of natural gas and light hydrocarbons (LPG) with oxygen or steam or an oxygen/steam mixture is mostly studied at this scope.

The key for pursuing high throughput systems, with fast response to transient loads, and low pressure drops, as well as compact configurations is represented by the use of monolithic catalysts with noble metal as active phase, operating at short contact times.

1.3 Features: Scope of this work

Concerning the reformer setup, the optimum in the reforming reactor configuration is catalyst bed of pellets with large external diameter and with high void fraction, in order to achieve maximum activity with minimum pressure drop [2].

The possible solutions to this structural need are for example catalytic rings or cylinder with several holes, or solutions based on the use of catalysts consisting of ceramic foams or, as underlined before in paragraph 1.2, monolithic structures.

Consequently, within this research, ceramic cordierite honeycomb monoliths, also in relation to their well-defined surface geometry (chapter 2.1), are chosen.

Supported or not supported by aluminium oxide layer, with or without catalytic loading, the monoliths are tested in a plug flow laboratory reactor (chapter 3.1).

The experiments are carried out with variation of the reaction conditions, like feed-gas composition, steam to carbon ratio, or temperature, and also of the structural parameters of the monolithic structure, like the channel openings, the reactor set-up configurations, or the different metal loadings.

One of the purposes of this work is to certify if the presence of a γ -Al₂O₃ washcoat layer may have an influence on conversions and selectivity of the hydrocarbons. This effect could be added to the well-known influences of the washcoat on the structure properties of the catalyst, such as higher pore volume, or larger active surface area, as observed in literature [10] and as already presented in chapter 2.

The study of the washcoat properties and of the influence of catalyst surface on the process activity is wide and varied: the literature includes studies about the reaction mechanism with the possibility of interaction between the steps in the gas phase and the surface (heterogeneous-homogeneous mechanism) [11], researches about the comparison of different crystalline phases of the metal oxide support, with attention on their catalytic activity and stability [12], as well comparisons of the different life of different supports [13], or tests of various supports, i.e. metal oxides or new materials like zeolites, concerning yields of hydrogen and by-products, underlining for example, the importance of the alumina support presence for the activity [14].

2. Materials

2.1 Monoliths:

Within this research, the basic materials for the preparation of the catalysts are ceramic monoliths of cordierite, magnesium iron aluminium cyclosilicate, with a honeycomb structure characterized by varying number of channels, calculated in cpsi (channels per square inch).

This well-defined structure of the cordierite is the main reason for the use of such a material. In fact the presence of regular and periodic structures, where the gases run, and defined channel dimensions, is a facility for the simulation of the process.

The possibility of process simulation is, as it will be explained, one of the most fundamental purpose of this research.

The cordierite is moreover the standard material in commercial and industrial catalysts production.

On the surface of this ceramic material is usually loaded the catalytic active materials, which in this case is represented by nickel metal. Nickel is here selected because, such as the cordierite, it is typically used in the industrial circle, and that increases the importance of this study.

The main properties of the ceramic cordierite are reported here below:

•	Chemical formula:	$(Mg,Fe)_2Al_4Si_5O_{18}$		
•	Thermal capacity [15]:	543-1387 J/(mol K)		
•	Thermal conductivity [16]:	1.5-2.5 W/m/K		
•	Porosity [16]:	0.5 max.vol%		
•	Density [16]:	$2.1 (g \text{ cm}^{-3})$		

As said, the choice of the cordierite monoliths is mainly due to the easier modelling of the process. Catalysts however consist usually of two or more components, assembled in the desired structure.

The basic structure of the catalyst is usually either a metallic support (oxides in the normal cases) or zeolites or mesoporous materials [17].

Within this research, a γ -Al₂O₃ layer, the so-called washcoat, is chosen.

2.1.1 Catalyst bed characterization:

The characteristic parameters of a honeycomb monolith bed are presented in figure 2.1:



Figure 2.1: characteristic parameters

where:

 d_{cell} : the side of the quadratic cell, representing the monolith channel side

s: the wall thickness of the channel

d: the monolith diameter

As seen in previous works, and through the definition of hydraulic diameter d_h , it's possible to see that the diameter of the cell, i.e. the side of the channel, coincides with the hydraulic diameter exactly.

$$d_{h} = \frac{4 * A_{P}}{P_{wetted}} = \frac{4 * d_{cell}^{2}}{4 * d_{cell}} = d_{cell}$$
(2.1)

where A_p and P_{wetted} represent the cross sectional area and the wetted perimeter for each channel respectively.

According to studies made in chapter 4.1.4.1, about the influence of the channels diameter on the activity, the specific surface area and the void fraction are here defined:

$$d_{cell} = d_h = \frac{4 * A_P}{P_{wetted}} = \frac{4 * (cross.area)}{(wett.perimeter)} = \frac{4 * \frac{(cross.volume)}{(tot.volume)}}{\frac{(wett.area)}{(tot.volume)}} = 4 * \frac{\varepsilon}{a_s}$$
(2.2)

and consequently:

$$a_s = 4 * \frac{\varepsilon}{d_h}$$
(2.3)

where the a_s is the specific surface area (m²/m³) and ε is the void fraction, defined as the ratio between the channels volume and the complete monolith volume:

$$\varepsilon = \frac{V_{void}}{V_{tot}} = \frac{d_{cell}^2}{\left(s + d_{cell}\right)^2}$$
(2.4)

2.1.2 Washcoat:

As said before, the preparation of the catalyst usually happens through the use of "building blocks" [17], represented by support materials (normally silica or alumina) or other compounds.

That means that in this work, there is the possibility to use two different reactor configurations: either simple nickel ceramic monoliths, where the active metal compound is directly loaded on the cordierite surface, as explained before, or the configuration with oxide support, where the catalyst structure is obtained with a support (γ -alumina/washcoat), with the

active component (nickel active metal) loaded onto this material, creating the so-called "supported catalysts".

The importance of the support is due above all to the maximization of the surface area of the active phase. In fact, generally the presence of the support provides a larger surface area than in the case of simple and unsupported cordierite, such as underlined in literature [10], where it's possible to notice a remarkable variation of pore volume and above all of the total surface. One can say that the support is a "vehicle" for the active phase. With the γ -alumina the surface areas can be in the range of 100-800 m²/g [17].

The research and the comparison are really important in order to study the activity of these supports, such as the γ -alumina, as it will be shown in the next chapters.

Indeed the support is supposed to be catalytically inactive by itself, or, only in partnership with the active phase, it can have an important role in the reaction.

Through the comparison of the different configurations and the study of activity in absence of active metal compounds, it's possible to certify this theory.

A similar research was realised also in other cases [18, 19], where the attention was focused either on the comparison of different supports effect, with an analysis also of the support oxides activity without active metal phase [18], or on the influence of different "washcoat" loading [19].

In [19] is underlined for example, the bright activity difference between the non-washcoated catalyst and the others with varying alumina loading, above all in the hydrogen selectivity, with differences sometimes nearly 20% selectivity (partial oxidation experiments).

The dates found in literature [18] certify moreover the remarkable influence of the aluminium oxide presence on the surface area dimensions, which is the highest, in comparison with other supports.

Still low and inaccurate is however the knowledge of the influence of the washcoat on the mechanism of the catalytic reaction, its personal catalytic behaviour and the relationship between the surface properties and the performances of the materials.

For this reason is particularly important this research, in order to better understand the supports properties, providing some clarity regarding their influence on reaction mechanism and accordingly on reaction products.

2.2 Catalyst preparation:

The preparation technique of the supported or non-supported catalysts and the accuracy of this technique are very important, in order to obtain a precise interaction between the active component and the surface of the carrier, either the simple ceramic cordierite or the γ -alumina supported monolith.

The precise interaction is necessary above all in the case of the washcoated-catalysts, in order to allow the specific properties of the aluminium oxide, such as the relatively high dispersion and the high degree of the thermostability of the catalytic component.

The ways for the preparation of the catalysts are basically two:

- a selective removal of a component from a phase containing the active component and the support (coprecipitation)
- a separate application of a precursor of the catalytically active material on a preexisting support (impregnation and precipitation)

The choice of this two different ways is bound with the loading of active component one will reach: in the case of cheap metals or support, i.e. with the aim of maximum active surface area per unit volume, the first strategy will be advantageous. If the purpose is to prepare very small particles with maximum utilization of their surface, the impregnation is the best method.

In this work, the way that has been followed for the preparation of the nickel catalysts here used, is an impregnation with a nickel nitrate solution, both with and without the presence of washcoat.

The preparation of the alumina layer on the basic ceramic monoliths belongs to an industrial project, i.e. this research develops and studies only the surface covering of the active nickel metal components.

Within the use of the washcoated-materials, usually with powdered supports is used a volume of solution larger than the pore volume in order to fortify the adsorption of the precursor on the support ("wet" impregnation).

With a preshaped support an "incipient wetness", "dry" impregnation is used, in which a just sufficient amount of solution is loaded, so that the exact pore volume of the carrier can be filled.

As said before, for this research are prepared nickel catalysts with different metal loading, i.e. 3w-% as well as 5w-% and 10w-% nickel charging.

The solution used is a nickel nitrate solution, exactly $[Ni(NO_3)_2 * 6H_2O]$ diluted in ethanol, with a nickel molar concentration of 0,05 mol/V.

The process for the catalysts preparation begins with the cradle of the simple unloaded monoliths: through the weight of every monolith ($m_{monolith}$), the molar concentration (c) and the desired metal weight percent (w-%), according to the following equation, it's possible to calculate the solution volume for every case.

$$V[l] = m_{monolith} \cdot \frac{w}{(1-w) \cdot M_{metal} \cdot c}$$
(1)

In order to improve the capability and the accuracy of the covering of the patterns, every monolith is prepared separately from the others.

In small test-tubes, the monoliths are submerged with the solution volume and left in a small furnace at 60-80°C under pressure, in order to evaporate the ethanol in the solution.

At the end of the first drying, when the first portion of ethanol is evaporated, on the surface of the monoliths the presence of a residuum, of a solid sediment is observed.

That means that the preparation needs successive dilutions with ethanol or with distillate water, followed by consequent new evaporations, in order to obtain a uniform loading of the nitrate of the catalytic active metal, even if the possibility to loosen the residual nitrate is sometimes not so easy, and it is necessary to repeat the procedure of the impregnation several times.

After the impregnation process, the so obtained catalysts were also subjected for several hours to calcinations.

A summary of the major characteristics of the prepared catalyst, that is also a small explanation of the passages for the preparation, is reported in the chart below.

monolith	loading	monolith	weight [g]	weight [g]	loading
number [%]		structure	without loading	with loading	[g]
1	10-w %	washcoat	0,56	0,7605	0,2005
2	10-w %	washcoat	0,5828	0,7808	0,198
5	5-w %	washcoat	0,5953	0,6689	0,0736
6	5-w %	washcoat	0,585	0,6632	0,0782
7	5-w %	washcoat	0,5781	0,6658	0,0877
8	5-w %	washcoat	0,6318	0,7263	0,0945
9	5-w %	washcoat	0,5531	0,6281	0,075
10	5-w %	washcoat	0,5782	0,6583	0,0801
11	10-w %	no-washcoat	0,4087	0,5269	0,1182
12	5-w %	no-washcoat	0,3871	0,439	0,0519
13	5-w %	no-washcoat	0,3882	0,4404	0,0522
14	5-w %	no-washcoat	0,3955	0,4454	0,0499

Chart 2.1: Catalysts preparation (the weight of the catalysts is taken before the calcinations)

2.3 Characterization techniques:

In this work, the catalysts prepared and used in the experiments, are completely characterized, in order to underline their properties.

This characterization is made in order to understand the behaviour of the catalyst, and to justify the obtained experimental results.

So the outputs can be bound to an explication and a study of the size of the catalytic active area. Basic is also the control of the real metallic composition, obtained following the preparation procedure of the catalysts, in order to see if the steps and methods used have been correct.

For this reason two different characterization methods, like BET analyses, and XRD analyses, have been carried out.

These researches give the possibility to know which composition and state, the catalyst has during the experiments. Especially with XRD analyses there is also the potential to understand how the catalyst structure is changed after the reaction.

With BET analyses, there is the possibility to see the changes in the surface size, due to the application of washcoat, compared to a normal cordierite monolith.

2.3.1 BET analyses:

BET is short for Brunauer, Emmet, Teller, the developers of BET-theory.

BET method is a common analysis process for surface's sizing, especially for porous materials, applying gas adsorption.

Brunauer, with Emmet and Teller, in their study, [20] have carried out many tests with very different gases, like nitrogen, oxygen, argon, carbon monoxide and dioxide, on some thirty samples of catalysts, catalyst supports, and miscellaneous materials.

On all these substances, the tree researchers have obtained the so-called S-shaped isotherms, that give the possibility to see and to compare the pore volume (or volume of gas adsorbed) with the pressure used.

The gas, normally nitrogen, is conducted over the sample. By cooling with fluid nitrogen

(-196°C), the gas molecules are immobilized (and stop swinging); so they use less of the for adsorption available surface. That allows to adsorb more gas molecules too, and admits a lower pressure.

While, heating the sample, a part of the adsorbed gases dissociates from the surface, and that gives the possibility to obtain the adsorption-desorption-isotherms.

For identified pressures happens in fact that the gas amount is proportional to the material's surface.

These examinations should emphasise and underline the structural difference between the cordierite monoliths without washcoat coating and the monoliths loaded with γ -aluminium oxide (Al₂O₃).

The washcoat is coated on a 900 cpsi honeycomb-monolith (cpsi means "channels per square inch").

When one compares the two different BET-lines, and calculates the surface area, in the case of the aluminium oxide coated monolith, it results larger (58.25 m^2/g) than the surface area of the "normal" cordierite (1.68 m^2/g).

This result certifies and validates the assumption that the washcoat presence multiplies the contact area of the unloaded cordierite.

In figures 2.2, the BET isotherms, obtained in the analyses, are reported.







Figure 2.2: BET isotherms a) bare Cordierite, b) washcoated Cordierite

2.3.2 XRD (X-ray Diffraction) analyses:

The powder diffraction method identifies the crystalline phases by diffraction of X-rays on the atomic planes.

The crystalline bulk consists of a regular order of atoms, ions, or molecules.

Due to this structure's periodicity, the crystals serve as three-dimensional diffraction pattern for suitable wavelengths.

The reflection is not possible in all cases, only in specific ones, where defined orientation among the crystal, the radiations' stream and the detector occurs.

X-ray diffraction is only possible if the conditions for a constructive interference, described by the BRAGG'S equation, are satisfied:

Bragg's law:

 λ = wavelength $n\lambda = 2 \sin \theta$ with: d = atomic plane distance θ = diffraction angle

In the first measurement the washcoat coated cordierite, without active catalytic loading, has been analyzed and the position and relative length of its peaks satisfy the values in the database. The database confirms also the cordierite data (figure 2.3).

Then a catalysts with 5-w% nickel has been analyzed. The preparation process includes calcinations and reduction, as said.

Two different XRD analyses (figures 2.4-2.5) of the same pattern were implemented, in order to deepen the study of the different phases present on the catalyst surface.

Figure 2.4 shows clear peaks for the active Ni metal phase and for the washcoat layer. Small peaks of predicted NiO are observed.

The second analysis (figure 2.5) has been performed with the same catalyst, but a different range of angle (normally the range is $15^{\circ}-75^{\circ}$, in this case only $35.5^{\circ}-50^{\circ}$) in order to measure for a long time and obtain a better analysis. The increased measurement time per degrees, decreases the typical analyses noise and improves the real peaks. This second analysis is also compared in figure 2.5 with the previous no-catalytic washcoated cordierite analysis.

The third analysis (figure 2.6), was carried out over a new sample produced under different conditions: instead of three hours, like the first sample, the second one has been reduced, after the calcination, for fifteen hours.

The analysis in figure 2.6, shows at first, that a second calcinations, in this case, is not necessary, since nickel-nitrate peaks are not observed.

In addition, this analysis, compared with the others, shows better and higher peaks for the metallic phase and the γ -aluminium oxide support, and very low traces of NiO.

The second reduction results anyway, in better crystallization of the metal so that the peaks are clearer, more visible and better defined, especially the ones of metallic nickel phase.



Figure 2.3 : XRD analysis, washcoated cordierite



Figure 2.4 : XRD analysis, 5w% Ni washcoated catalyst



Figure 2.5 : XRD analysis, 5w% Ni washcoated catalyst, different range of angle



Figure 2.6 : XRD analysis, 5w% Ni washcoated catalyst, longer reduction

3. Analysis and testing procedures

3.1 Testing rig:

The experimental activity consisted of tests of methane/ethane/propane SR and CPO/ATR.

The experiments were carried out with a testing rig, specifically designed to feed both gaseous and vaporized components and to investigate monolithic catalysts.

An overall scheme of the rig is reported in figure 3.1: three sections are presented, namely feeding section, mixing section, the reactor section and the analysis section.

The feeding section consist of several MFC, which regulate the flow of the gaseous species, fed from high pressure cylinders.

The gases argon, methane and oxygen as well as calibration gas mixtures come from company Air Liquide (Messer Griesheim GmbH in former times).

Supplied gases are dosed by four F-201C mass flow controllers (Fig. 3.1: MFC1-4) manufactured by company Bronkhorst Hi-Tec. These mass flow controllers can ensure a gas flow between maximal 0,5 l/h und 5 l/h depending on construction.

The water supply from the reservoir, in which distilled water is kept ready at an overpressure of 3 bar, is regulated by a flow meter Liqui-Flow (Fig. 3.1: LFC) produced by the same company. Here the maximum value is about 5g/h (i.e. steam of 6.2 l/h).

LFC is controlled by the analogue E-5752 and the four F-201C MFCs are controlled by the digital E-7000 "evaluation and control system", both also produced by company Bronkhorst Hi-Tec. Online controlling of the E-7000 control system is possible, too, with the aid of the program Flow-View installed on the measurement computer.

The liquid stream is downstream vaporized and at the same time mixed with gaseous stream, in the vaporizer-mixing chamber, present after the LFC, as shown in figure 3.1.

The temperature of the vaporizer, of the furnace and of the heated pipeline sections, between vaporizer and reactor or, between reactor and cold trap, are monitored by the 818S universal controller, manufactured by company Eurotherm (Fig. 3.1 to 3.3: TI = temperature indicator, TIC = temperature indicator and controller).

In order to improve and to provide an exhaustive analysis of the products, the reaction system is directly connected with the analysis sector, consisting of a gas chromatograph and a mass spectrometer, with a cold trap and a silica gel trap for the condensation of produced or notconverted steam.

For security, check valves, manufactured by company Swagelok are used. They avoid a propagation of the ignition, in different areas of the reactor system. A pressure control valve produced by the same company, provides further security at the reactor exit. In the case of too high pressure each apparatus is automatically switched off by a Baratron P-switch, manufactured by company Bezner

Figure 3.1 tries to give a first view of the plant, trough a complete flow chart, both for partial oxidation experiments and steam reforming/autothermal reforming setup.



Fig 3.1: Flow chart for CPO, SR and ATR setup

The different gas feeds, with the own digital control (mass flow control for the gases and liquid flow control for water), but also the different temperature controls and detectors of vaporiser, reactor and pipes, and the analysis area with the own argon feed, are here displayed.

The different system settings, either for the steam reforming experiments or for the catalytic partial oxidation ones, are defined in the next sections of this chapter.

In each case, in the different figures, the used equipments and lines are red pointed out.





After the digital flow control unit, the gas mixture reaches a three-way valve, where the feed can be divided in two different streams, one in a small simple mixing chamber, that allows also the exploration of non-stationary phenomenon, and a second in a vaporizer, as said, used as mixing chamber too, typical for the so known "wet-experiments".

In figure 3.2, the settings of the reactor system for dry processes, such as the catalytic partial oxidation are displayed. The three-way valve allows to carry the gases trough the small

mixing chamber and then in the reactor, where the gases through the enclosing oven are warmed up.

After the reaction the gases are directly lead to the analyses, either with the "quadrupole" mass spectrometer or the gas chromatograph.

In the investigation of the "wet processes", such as the steam reforming or the autothermal reforming experiments, a larger volume in the mixing chamber is necessary. There is the necessity in this case to produce a large quantity of steam.

The vaporizer is filled with stainless steel. This device, together with the larger volume, allow an higher surface and so that a pulseless water evaporation. This configuration for steam reforming and autothermal reforming is shown in figure 3.3. In the vaporizer, water is evaporated at 200°C, and mixed with the other reactants. At the end, all the gases are carried to the reactor chamber through a pipe heated at 150°C. After the reactor, the unconsumed water is condensed through a cold trap, and the dry gases carried either to the mass spectrometer or to the gas chromatograph.





3.2 Reactor:

The Plug-Flow-Reactor typology, used here for this plant, guarantees the short contact times between gases and catalyst.

The presence of the oven provides the regular heating of the catalyst, and plays also the role of barrier for the temperature transport with the external environment.

This reactor setup allows both an available, pulse-free addition of steam for the steam reforming experiments, both an easy inspection of the plant.

This setup and the analysis instruments are also suitable for future experiments with high hydrocarbons.

The first important peculiarity of the reactor system is to supply to the reaction chamber several gases at the same time, in different conditions of amount, above all in presence of varying temperatures of the reactor, and the possibility at discretion, to carry the activity repeatedly in an experiments section.

Besides the varying blends of the reactants, such as in the second chapter underlined, in these experiments it's interesting to use and test several types of catalysts, different for charging and length.

For this reason the possibility of a simply catalyst substitution, without a full rebuilding of the installation, is really necessary.

The reactor consists of a Pythagoras ceramic pipe with an external diameter of 38.5 mm and an internal diameter of 30 mm (Fig. 3.4). The ceramic pipe is closed by two flanges, as shown in figure 3.5.

Only six hexagon socket must be removed in order to open one of the flanges, to take out the catalyst holder.

The flanges can be taken to a certain temperature with the aid of a thermostat manufactured by the MGW Lauda K5. In our case they are kept at 110°C by ethylene glycol produced by company VWR.



Fig 3.4: Construction view with reactor scheme [21]



Fig 3.5: Flanges construction view

The catalyst holder consists of two parts (Fig 3.6 a), a Pythagoras ceramic pipe (internal diameter 8 mm; external diameter 20 mm) and one component made of fired pyrophyllite (Fig. 3.6 b). These components serve as something like a cup containing the monoliths at the bottom and at the top they appear like a cap, consistent with the cup below.

Up to five several 1cm monoliths can be placed in the catalyst holder pictured in figure 3.4. Usually the monolith catalyst is placed in the central position, between inert sections of two monoliths (heat shields).

A ceramic band (thickness of 1 mm), around the catalyst prevents a possible bypass.

In figure 3.6, an old catalyst holder configuration is presented: in this configuration three monoliths being 1 cm long could be placed in this catalyst holder.

The actual configuration, shown in figure 3.4, presents the possibility to load, in the reactor chamber five monoliths (diameter 15mm, length 10 mm).



Fig 3.6: Construction view: a) upper and lower catalyst's owner b) dimensioned representation of the reaction chamber

Temperature measurement below and above the catalyst is taken by a Rh/Pt-thermal element type S, which is connected with the read out unit Fluke 54 II. The arid flows at the reactor exit are controlled by the Intelligent Digital Flowmeter produced by company Varian. The quadrupole mass spectrometer (QMS) allows a continuous and transient (t < 100 ms) analysis of the reaction products. Additionally, in the case of steam reforming the water leaving the reactor is condensed out in a calibrated cold trap in an ice bath. The installed gas chromatograph Varian CP-3380 represents additional analytical equipment.



Fig 3.7: Reactor temperature profiles

Temperature measurements had been previously performed in the empty reactor with a sliding thermocouple.

Figure 3.7 reports some results at different set-point values of the oven T-controller.

Along the whole length of the oven, the temperature profile was not flat; however a nearly isothermal zone was established between the coordinates 18-24 cm (measured from the bottom).

Accordingly with this result, the sample holder and the monolith catalysts were located within this zone.

4. Experimental results

4.1. Steam-reforming of C_1 - C_3 hydrocarbons over ceramic monoliths. Study of the homogenous reactions:

As above said, steam reforming of hydrocarbons is the preferred process for hydrogen and syngas nowadays, and for this reason an important portion of this research is related to a consolidation of the knowledge about the efficiency of the SR-technique.

Previous studies and experiments dealt with the catalytic steam reforming processes, carried out over 900 cpsi honeycomb monoliths, coated with rhodium, and obtained within an industrial project. The conversion of light hydrocarbons, namely methane, ethane and propane, and the composition of the products mixtures were analyzed at varying operating conditions, with pressure of 1.013 bar, gas hourly space velocity of 40000 1/h and always with 75% of inert argon in the gas feedstock.

Those original studies are herein extended by the analysis of the possible non-catalytic contributions to the process chemistry.

In the following, the main results of the previous catalytic experiments are first reviewed. Then, the results of the experiments in the absence of catalyst, will be illustrated and compared with the expected performance of a pure gas-phase PFR reactor.

The intention is to see how the mechanisms of the homogeneous reaction may influence the normal catalytic steam reforming process [11] in order, as said at the beginning, to develop specific and detailed computational codes.

Both the selectivity, and the conversion, shown in the next figures, are plotted vs. the reaction temperature, measured at the end of the reactor, downstream the catalytic reaction chamber.

The selectivity of the catalytic experiments here below described, as well the future analyses, because of the possibility of the analysis devices, i.e. gas-chromatograph, to check only dry gases, are normally obtained by products yields, descending from carbon balances.

4.1.1. Steam reforming of light alkanes over Rh-coated monoliths:

Figure 4.2 reports the results of the methane catalytic steam reforming experiments, describing the conversion trend and the product selectivity.



Figure 4.2: Conversion of CH₄ and selectivity products profile, catalytic SR (*Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation*)

The conversion of methane was appreciable at about 400°C and progressively increased with the temperature. 90% conversion was reached at about 850°C.

Through the plotted data, it's possible to see that the methane conversion was really restricted by the thermodynamics of the reforming reaction: as underlined in literature [2] in order to achieve maximum conversion rate, the reaction must be carried out at very high temperature (800-900°C), and low pressure. The experiments results, shown in figure 4.2 a), seemed to certify this situation.

In figure 4.2 b), the selectivity profile is plotted: the carbon dioxide production was always preponderant in comparison to the carbon monoxide trend. At high temperature, even if the selectivity to carbon monoxide slowly rose, the carbon dioxide presented still high values (60-70%), around 800-850°C, and anyway higher values than the other product.



Figure 4.3: Conversion of C₂H₆ and selectivity products profile, catalytic SR (*Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation*)

The trend displayed by the experiments carried out with ethane is really interesting: the conversion reached high values, 70-100% conversion respectively, at very low temperature, around 500-600°C, and maintained these high values for a large range of temperature, until 900°C. Interesting was the quite perfect agreement of the experimental results with the trend of the chemical equilibrium.

By the products selectivity trend, at low temperatures (400-600°C), the ordinary carbon monoxide and carbon dioxide production was accompanied by small percent of methane, between 20-30%, and, at the same time, by very low quantities of acetylene. This compounds slowly disappeared, with increasing temperature, allowing the formation of higher percent of carbon dioxide, and above all carbon monoxide at very high temperatures (70%).

In figure 4.4, the propane conversion trend is presented: the conversion rate displayed by the experiments using propane as feedstock, at low temperature (400°C) seemed to be lower, in comparison to the ethane conversion data, even if, at high temperature (from 600°C), the values were the same and they were comparable.

Indeed the conversion of propane in the catalytic experiment, carried out through the Rhcatalyst, was appreciable (20% conversion) at about 300-400°C, and drastically increased with increasing temperature, until 600°C, where the trend presented in figure 4.4 a), reached the complete conversion, maintaining then a quite constant profile also for higher temperatures.

Analysing the different experimental profiles presented in figures 4.2, 4.3 and 4.4, it's possible to see how the two experiments, carried with ethane and propane feedstock, showed, in comparison with the methane one, anyway a faster and easier hydrocarbon molecules activation, displayed in figures, for example, by the easier (in terms of temperature) consumption of the hydrocarbon reactants.

In figure 4.4 b) the results in C-selectivity of the products by catalytic steam reforming of propane are presented: the results were quite similar to those obtained in methane steam reforming, with a clear tendency to carbon monoxide and carbon dioxide, with the exception here, of a light production of methane, above all at low temperature, around 400-550 °C.

This light production of methane is followed by a reduction of the carbon dioxide selectivity, as illustrated by carbon dioxide and methane trends in figure, showing a parallelism between the two compounds, above all at temperatures corresponding a few carbon monoxide quantity.


Figure 4.4: Conversion of C₃H₈ and selectivity products profile, catalytic SR (*Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation*)

Through this small analysis of the catalytic experiments, it's now easier to compare these results, obtained in previous works of this institute, with the next results of the gas-phase reactions, trying, as said at the beginning of this chapter, to study the influence of the homogeneous reactions on the productivity of the steam reforming processes carried with catalyst monoliths.

The implementation of new and precise software, able to reproduce the real process conditions, the behaviour and the activity of the catalysts used in the experiments, urges the necessity to understand the influence of the support presence on catalyst activity and process mechanism and products too.

All that clears the attention and the interest in the following paragraphs to analyse and compare different gas-phase experiments, carried either with uncoated cordierite ceramic monoliths, or with ceramic cordierite coated with aluminium oxide.

In each analysis, the experimental results are accompanied by a comparison to the theoretical simulation issues of the homogeneous reaction.

The experiments have been performed with different feedstock, as well the catalytic ones, respectively methane, ethane and propane, to show the varying reactivity in presence of different hydrocarbons.

4.1.2. Methane:

Steam reforming experiments were performed under the same operative conditions as those used with the catalytic phase.

This methane steam reforming mixture were fed to the same reactor assembly used in the previous catalytic experiments, with the only difference that in the reactor configuration (chapter 3.2) for the homogeneous reactions, the catalytic coated monolith used in the heterogeneous phase, is replaced by an uncoated blank cordierite monolith, which can be also supported by an aluminium oxide layer.

In figure 4.5 an example of the reactor configuration is reported.



Figure 4.5: monolith reactor set up

As said before, and like previous works, concerning the analysis of the effect of varying monolith metal loadings on hydrogen and syngas selectivity, in different processes, like "catalytic oxy-reforming of methane" (CPO) or "oxy-steam reforming of methane" (ATR) [22], this study tries to underline the influence on the process productivity of different steam to carbon ratios, and the effect of the presence of an alumina support.

Large excess of steam was used, as commonly made in varying works in literature [2, 3, 5].

Indeed, as observed in other researches [23, 24], although the stoichiometry of the steam reforming reaction of methane requires only 1 mol water for each mol methane, normally an excess in the steam content (S/C ratio of 2.5 or 3) is used, in order to reduce the by-product carbon formation, in according to the Boudouard reaction (chapter 1.3., E.5) and the methane decomposition (chapter 1.3., E.6).

In particular, steam to carbon ratios of 2.5 and 4 were adopted, as already done and described in precedent theses on the same theme [21].

In figure 4.6, the methane conversion trend, obtained by homogeneous phase steam reforming experiments, with supported and not supported cordierite monoliths and different steam contents, is plotted.



Figure 4.6: Conversion of CH₄, CH4-SR gas-phase

At a first analysis of the picture above, there is no great difference between the experimental results, with, on the contrary, fast a perfect analogy among the different performances, in spite of the varying steam content and the different monolith structure.

In the absence of a catalytic phase, the conversion of methane is appreciable ($\sim 10\%$) at about 1050°C and rises with temperature increasing to 50% at about 1150°C.

The quite inexistent difference among the experimental results, as said above, underlines that neither the steam to carbon ratios nor the presence of a washcoat layer seem to affect the performances in the homogeneous reaction.

The theoretical results deviate the experiments, showing a slower conversion, according to the temperature reaction, with traces of converted hydrocarbons only at very high temperature (>1200°C).

The low conversion plotted in the figure above, seems to certify an other time, the low activity of the methane molecule in presence of water and high temperature, associated, as said in the previous paragraph, to the strong bond energy, representative the C_1 -compounds. However is clear the difference between the trend of the homogeneous reaction results and the results obtained with rhodium coated monolith, where the catalyst presence is translated in a faster and higher conversion, according to the temperature reaction.



Figure 4.7: Conversion of CH₄, catalytic SR

(Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation)



e,0 **s**

0,4

0,3

0,2

0,1

1300

1100

1200

1000

0 -

400

500

900 cpsi honeycomb monolith

700

600

800

T [°C] (End Reactor)

900

1000

1100

1300

1200



. 0,5

0,4

0,3

0,2

0,1

0

400

500

600

700

800

T [°C] (End Reactor)

900

Figure 4.8: Selectivity products profile, CH₄-SR gas phase

The measured product distribution is reported in fig 4.8 a)-e), in terms of C-molar selectivity. Carbon monoxide, carbon dioxide, ethane and other C2 hydrocarbons are mainly observed. At temperatures below 800°C (that is at extremely low conversion of methane) carbon dioxide is practically the unique C-containing product. Its selectivity decreases dramatically down to about 10% at increasing temperature up to 1000°C (with conversions of methane in

the order of 5-10%).

Within the intermediate T range 800-1000°C (wherein the measured methane conversions increased from 1 to 10%) ethane is also detected in the product mixture with a bell-shaped trend.

Carbon monoxide is instead the most important product at higher temperatures and higher methane conversions.

Small amounts of ethylene and acetylene are also measured around and above 1000°C.

Steam to carbon ratio little affects the product distribution.

Instead an effect, though small, is played by the presence of a washcoat layer. The aluminium oxide coated monolith, in fact, gives rise to higher COx selectivities and lower ethane selectivity.

Figures 4.8 a)-e), as figure 4.6, also report for comparison the calculated conversion of methane and product distribution of a purely homogeneous plug-flow reactor.

The simulations are performed with the computer package for DETailed CHEmistry Models (DETCHEM), by assuming the same operating and geometric configurations (T, feed flow rate, S/C, reactor length, and channels opening) as those of the experiments.

As seen in fig. 4.6, the measured amount of converted methane exceeds that predicted on the basis of the gas-phase chemistry.

The calculated trend is shifted to higher temperatures, with a gap between measured and calculated conversion of nearly 150°C.

This could be interpreted littler assuming that during the experiments, methane reacts within a larger volume than that of the monolith channels which was considered in the simulations, or that the process is somewhat promoted by the presence of the bare or washcoated monoliths.

In the latter case, data could be explained by an effect of "radical seeding" of the monolith wall, that is a release of radical species (formed on the surface by dissociative adsorption of the molecular reactants) from the non-catalytic wall to the bulk.

Such an issue (weather a catalytic surface can interact and even start a gas-phase process) has been treated in the literature [25], in the case of fuel rich combustions.

Both experiments and modelling results tend, however, to exclude that the surface chemistry can effectively orient the gas-phase chemistry given the very limited amount of radicals that could desorb from an active surface.

That means that it's improbable that non-catalytic surfaces as those used in the present study could present an important promotion of the gas-phase chemistry.

However, some remarkable differences are found between measured and expected products distributions.

The calculation shows that in a purely homogeneous reactor, methane coupling to ethane is a primary reaction at initial methane conversion, while ethylene and eventually acetylene are major products at increasing conversion. The experimental results showed instead that carbon monoxide is the most abundant product at high conversion.

Since the presence of the washcoat (that is a high surface area wall) even enhances the selectivity to carbon monoxide, the comparison between measured and calculated products seems to suggest that surface partly influences the products distributions.

This result could be also interpreted assuming that the presence of the washcoat layer creates an "heterogeneous wall effect", causing the enhancement in the production of typical heterogeneous products, such as COx.

This heterogeneous wall effect could be descend from a particular activation, at very high temperatures, of the Al₂O₃ support, exhibiting a typical catalytic activity.

4.1.3. Ethane:

As underlined in other works [26], there is generally a clear and great interest in the research of the reactivity of hydrocarbons such as ethane and propane.

The interest consist, for example in studies of the behaviour of high hydrocarbons, contained in the natural gas used by solid oxide fuel cells, in order to examine the carbon formation on the catalyst surface, due above all to the decomposition of such hydrocarbons.

A large study of steam-reforming over nickel/alumina catalysts was performed [26], with ethane or propane respectively as inlet fuels, in order to find and develop of alternative catalysts, able to reform high hydrocarbons components with low degree of carbon deposition.

Ethane and propane represent indeed the main high hydrocarbons present in the natural gas.

Ethane reforming, such as propane reforming, is also studied as process for the formation of either methane-rich gases or of hydrogen, or hydrogen with carbon monoxide mixtures, with a particular attention to the problem of the carbon deposition on the catalyst [27]. In this case the research is led on coprecipitated Ni-Al₂O₃ catalysts, and tries to underlined that the reaction proceeds via surface carbon species, which then react with water and hydrogen.

In analogy with the methane/steam experiments, the reactivity of ethane/steam mixtures was also studied over non catalytic monolith, both bare and coated with a γ -Al₂O₃ layer.

As also in the methane/steam experiments 900 cpsi honeycomb monoliths were used, tested in a laboratory plug-flow reactor, in presence of pressure of 1.013 bar, gas hourly space velocity of 40000 1/h and always 75% of inert argon in the gas feedstock.

Conversions and selectivity of the experiments, carried either only with blank ceramic cordierite or with alumina coated cordierite, are compared in each figures with the simulations of a purely homogeneous reactor.

The experiments were carried out with a steam to carbon ratio of 2.5. The selectivity were plotted as function of the ethane conversion.

This representation makes more immediate the comparison with the expected output of a gas phase process.



Figure 4.9: Conversion of C₂H₆, C2H6-SR-gas phase

The ethane conversion in figure 4.9, both by experiments and by theoretical data, begins to rise around 700°C. By increasing temperature, the conversion grows drastically, reaching the maximum value at 900°C (~ 95%).

The experimental results are in perfect agreement with the expected values of the pure homogeneous reaction, both for the experiments carried out with bare monolith and for the experiments with γ -Al₂O₃ coated reactors. There is no evidence of "wall effects", due to the presence either of the monolith or of the washcoat layer.

This almost perfect analogy with the theoretical results, is a certification of the precision of the simulation mechanism and software here used and an important step for the computational codes development.

Figures 4.10 a)-c) and 4.11 a)-b) report the distributions of the C-containing species and compare them with the reference case of homogeneous reactor.



Figure 4.10: Selectivity products profile, C₂H₄, C₂H₂, CH₄, by C₂H₆-SR gas phase



Figure 4.11: Selectivity products profile, CO, CO₂, by C₂H₆-SR gas phase

With the selectivity products analysis, there is above all the intention to see if the alumina support presence may have an impact on the products distribution, even if the conversion trend, as underlined, was not influenced.

The ethane conversion, in pure homogeneous conditions, proceeds through radical reactions. The chain initiation could be represented by the decomposition of an ethane molecule in 2 methyl ones, with an activation energy of about 88 kcal/mol:

$$CH_3CH_3 \rightarrow 2CH_3 \tag{4.1}$$

The chain propagation steps, concern the attack of a molecule of methyl to a second molecule of ethane, with the formation of methane and ethyl radicals, which can then react, giving olefins, such as ethylene and other radicals:

$$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2$$

$$(4.2)$$

$$CH_3CH_2 \rightarrow CH_2CH_2 + H \tag{4.3}$$

Analysing figures 4.10, it's possible to see that the ethylene represent the major product, among the C2 products. In fig. 4.10 a), its selectivity shows very high values at low ethane conversion, and then decreases drastically, with increasing conversion.

Acetylene and methane represent instead the secondary products, both with increasing selectivity at increasing ethane conversion.

Acetylene begins to present appreciable results at 60% ethane conversion. At 80% conversion, its selectivity shows values around 10%, how the predicted results of the pure homogeneous reaction, and then increases drastically when the ethane conversion reaches its maximum value.

The selectivity to methane is very low, and presents appreciable performances only at very high ethane conversion grade. Its selectivity seems to be slightly enhanced by the presence of the cordierite or of the γ -Al₂O₃ coated monolith.

In figures 4.11 a)-b), the selectivity to carbon monoxide and carbon dioxide is plotted.

The calculation shows that, in pure homogeneous reaction conditions, the selectivity to carbon oxides is quite inexistent. The experimental results, instead, present low selectivities, but only when the ethane feedstock is almost complete converted.

For the carbon monoxide and dioxide production, the experimental values are not higher than 25% for the first, and 10% for the second.

Except for some data obtained at 20% ethane conversion, visible by ethylene and acetylene profiles (maybe affected by some experimental errors), the measured products distributions, observed over the uncoated monoliths, show a very good match with the model prediction.

In the presence of washcoat coated monoliths, slightly higher ethylene selectivity together with lower acetylene selectivity are observed.

Indeed the higher washcoat surface seems to enhance the chain propagation reactions, favouring then the ethylene and methane production, and at the same time, obstructs the acetylene formation.

In the analysis of the CO_x selectivities, the same remarkable differences, seen by methane/steam mixtures, are here, by ethane experiments, not observed.

In the case of ethane/steam experiments, the washcoat presence has no effect on the carbon oxides formation.

As made with the methane research, it's interesting to show again the values and the results obtained by catalytic ethane steam reforming, in order to better understand the difference of the activity in "catalytic" and "no-catalytic" conditions.



Figure 4.12: Conversion of C₂H₆, comparison between homogeneous reaction and catalytic SR (*Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation*)

Also by this comparison, as well by methane experiments, is clear the difference and the influence of the presence of the Rh-catalyst: at already 400°C the conversion shows values around 50% of converted reactant, and, above all, around 500°C reaches almost the maximum of the values, joined by homogeneous conditions, only at very high temperatures, as seen before in figure 4.9.

The analysis of the measurements made in presence of Rh-catalyst, and the comparison of them with the results obtained in figure 4.9 in no-catalytic conditions, underline that the homogeneous reactions and mechanisms, occurring in the monolith channels, could influence the normal catalytic conversion or products distribution, at temperature higher than 600°C.

4.1.4. Propane:

The effects investigated in this section are, at first the possible influence on conversion and product distributions of the variations in the channels openings and in the monoliths wall thickness, using two different ceramic cordierite monoliths, and then, as made with methane and ethane feedstocks, a comparison between the performances of bare and a γ -Al₂O₃-coated honeycomb monoliths and the results predicted by pure homogeneous reaction conditions.

4.1.4.1. Influence of channel dimensions:

The varieties and the possibilities of channel dimensions in the monoliths technique are numerous: the number of channels per square inch of the monolith surface (cpsi) varies, normally, between 100 and 900 unities.

In the next figures, the trends in conversion and selectivity of two different blank monoliths, of 100 cpsi (*monolith 1*) and 900 cpsi (*monolith 2*) respectively, are compared.

At first, through the chart below, it's possible to compare the different structural properties of the monoliths, concerning mostly, number of channels, channels diameter, wall thickness, specific surface area, void ratio and also diameter and length of the monoliths here used.

Cordierite Monolith Type (channels per inch ²)	<u>100 cpsi</u>	<u>900 cpsi</u>
Channels per mm ²	0,15	1,40
Channel diameter	2 mm	0.76 mm
Wall thickness	0.45 mm	0.07 mm
Specific surface area	$\sim 1330 \text{ m}^2/\text{m}^3$	$\sim 4410 \text{ m}^2/\text{m}^3$
Void fraction E	0.67	0.84
Monolith diameter	15 mm	15 mm
Monolith length	10 mm	10 mm

Chart 4.1: Monolith specifications

Using the dimensions of the channels diameter, together with wall thickness and monolith length, as already seen in chapter number 2, the specific surface area was calculated, and compared between the two different monolith types: the 100 cpsi monolith presents a lower specific surface than the 900 cpsi one.

Through the structural data shown in chart 4.1, it was possible to identify the void fraction for each monolith, representing the ratio between the volume of void channels and the complete volume (considering also the wall thickness).

As discovered in literature, the presence, on the surface of the monolith of an higher number of channels, characterized by lower openings and wall thicknesses, tends to enhance the void fraction, as underlined in chart 4.1:

 $\boldsymbol{\varepsilon}$ (100 cpsi monolith) < $\boldsymbol{\varepsilon}$ (900 cpsi monolith)

This enhancement in the specific fraction of voids, naturally may influence, at constant volumetric flow, the gas velocity in the reactor, with a decrease of its values and consequently the residence times of the process.

These data allow indeed, a study about the influence of channels dimensions on the residence time of the gases in the reactor, defined through the successive expression:

$$\tau = \frac{V_R}{\dot{V}}$$

where V_R represents the reaction volume, while V is the volumetric flow leaving the reactor. The reaction volume depends on the volume of the channels and, because of the definition of ε , seen in chapter number 2, consequently on the void fraction. An enhancement in the void fraction values, means an increase in the reaction volume, and then in the residence time.

 τ (100 cpsi monolith) < τ (900 cpsi monolith)

Hence, it could be interesting analyse the effect of this varying residence time on the activity of the experiments, in order to see if the channels openings variation may influence the results.



Figure 4.13: Conversion and selectivity, C₃H₈-SR gas phase

Analysing the literature [28], it's possible to see that the formation of olefins, like ethylene and propylene, in steam reforming of propane, by homogeneous conditions, could be regulated by a pyrolysis radical mechanism.

The chain initiation reaction in case of pure pyrolisis is

$$C_3H_8 \rightarrow CH_3 + C_2H_5 \tag{4.4}$$

which presents an activation energy about 85 kcal/mol. After the formation of the first radical, chain propagation steps are the H abstraction reactions, presenting an activation reaction of 98 and 94 kcal/mol, respectively:

$$\mathbf{R} + \mathbf{C}_3 \mathbf{H}_8 \to \mathbf{R} \mathbf{H} + \mathbf{n} \cdot \mathbf{C}_3 \mathbf{H}_7 \tag{4.5}$$

$$R + C_3 H_8 \rightarrow RH + iso-C_3 H_7 \tag{4.6}$$

and successive reactions of propyl radicals could form ethylene and propylene:

$$n-C_3H_7 \to C_2H_4 + CH_3 \tag{4.7}$$

$$n-C_3H_7 \to C_3H_6 + H \tag{4.8}$$

together with methane, formed by the attack of methyl radical molecule to a propane one:

$$CH_3 + C_3H_8 \rightarrow CH_4 + n - C_3H_7 \tag{4.6}$$

The first important result, seen analysing figures 4.13 **a**)-**e**), is the very appreciable agreement between the experimental results and the predicted pure homogeneous reactor performances.

About the products distribution, the main observed species are the typical predicted products by steam cracking, like olefins C_3 - C_2 , methane and acetylene. In the experiments analysis, the CO_x products are literal inexistent, and for that reason, in figures 4.13, there is no trace of CO_x analyses.

Indeed there is no really great difference between the two set-ups, at a first view. At low temperature, around 700-750°C, the monolith with fewer channels per square inch (100 cpsi) presents (figure 4.13 a)) slightly higher propane conversion than the other one (20% vs. 10%).

Between 750°C and 800°C this small difference disappears, while, after 800°C, the results of the conversion in the monolith 1, begin to rise slightly stronger than the 900 cpsi monolith, showing anyway a very light difference.

Normally, by propane steam reforming, as well by high hydrocarbons reforming, the cracking reaction is favoured, in comparison with the second reaction of dehydrogenation, producing propylene. In figures 4.13 b) and c), decreasing propylene selectivity, at increasing propane conversion, is accompanied by a slightly increase in ethylene production.

The methane selectivity, in figure 4.13 e), presents a quite constant trend, with values between 10 and 20% selectivity, and seems to attest the theoretical stability of the methane production by steam reforming process, due normally, to his own thermodynamic stability.

In terms of influence of the monolithic structure on the selectivity, the lower number of channels by the 100 cpsi monolith, enhances and slightly favours the ethylene and the propylene selectivities (figures 4.13 b) and c)), at high and low propane conversion respectively.

By methane trend, the 900 cpsi monolith presents higher values in comparison both with the monolith 1 trend and with the simulations data.

The olefins produced by high hydrocarbons reforming, may receive further reactions of decomposition and condensation. At very severe conditions, i.e. at very high temperatures, the decompositions reactions could help the formation of acetylene.

In figure 4.13 **d**), the two experiments present, at very high propane conversion, a low increase in the acetylene selectivity, which drastically arises at complete conversion, as also displayed by the pure homogeneous phase.

The results here analyzed show a very appreciable agreement between experimental data and predicted values. The products distribution and the conversion displayed by the experiments, follow the qualitative trend of the pure homogeneous process.

The analyses show no appreciable wall effects on conversion or selectivities profiles, which are also not influenced by the variation of structural properties, such as channels openings or wall thickness of the monoliths. The consequent alteration of the void fraction in the two different monoliths, doesn't seem to change appreciably the activity of the experiments.

4.1.4.2. Effect of the presence of washcoat support:

After this analysis over the influence of the geometric monolith parameters, i.e. channels dimensions, as already made for the previous hydrocarbons, i.e. methane and ethane, also for propane, there is the desire to see if it's possible to detect a positive influence and an improvement on hydrocarbons activation, productivity and selectivity, due to the use of a γ -alumina support, coated on the cordierite surface.

The conversion results are plotted in comparison with the temperatures, taken at the end of the monolith reactor. The selectivity values are compared with the conversions ones.

In order to deepen the analysis of the behaviours of the different monolithic configurations (with or without washcoat coating), and to improve the reliability of the results, for each structural configuration, two experiments are plotted, both carried out with the same operating conditions.

The experiments, as made for the other cases, are compared with the simulations of the pure homogeneous phase reaction over a 900 cpsi honeycomb monolith.



Conversion

Figure 4.14: Conversion of propane, C₃H₈-SR gas phase



Figure 4.15: Selectivity profile, C₃H₈-SR gas phase

These first analyses show that there is not a great difference between the uncoated cordierite and the washcoat coated monoliths performances, both in propane conversion and selectivity values (figures 4.14 and 4.15 a)-f).

By conversion trend, in figure 4.14, there is on the contrary, a really good agreement between the experimental performances and the results obtained with the simulations.

The propane, both by experimental tests and by the pure homogenous phase, begins to be converted at about 700°C, and its curve rises quickly to very high conversion values, reaching the maximum performance, already at 900°C.

In the selectivity trends, in figures 4.15 **a**) and **b**), both with and without the γ -aluminium oxide support, the experiments, at low propane conversion, in comparison with the pure homogeneous phase, present a low decrease and a light increase in the propylene and ethylene values respectively. In the same figures, but at high propane conversion, a perfect agreement between experimental and simulation results, is verified.

In figure 4.15 e), the selectivity to acetylene begins to present interesting values only at high propane conversion: it presents, by complete feedstock conversion, 60-70% selectivity for the pure homogeneous process, in comparison with the 20-30% selectivity of the experiments.

Analysing figures 4.15 c) and d), the experiments present slightly higher selectivity to methane and, at the same time lower selectivity to ethane, if compared with the pure homogeneous reaction.

The calculation shows therefore, that in a purely homogeneous reactor, ethylene and propylene are the main products, at initial propane conversion, with also appreciable quantities of methane. At increasing conversion, the ethylene slightly increases, while propylene drastically decreases and acetylene is detected. The experimental results, as seen, in each case seem to confirm these trends, especially in figure 4.15 **a**), **b**), for ethylene and propylene production at high propane conversion. The presence of the cordierite or of the γ -Al₂O₃ coated monolith, instead seems to enhance the selectivities to methane and at the same time to decrease the production of ethane and acetylene.

This fact could be interpreted considering a slight influence of the monolith surface (increased moreover by the presence of the washcoat), represented by a "quench" effect on the termination radical reactions (with the consequent decrease in ethane production) and on the decomposition reactions of ethylene and methane to acetylene.

4.2. Study of the activity of nickel/washcoat/ceramic monolith:

The research activity was extended to the analysis of the SR performances of Ni-coated monoliths. At this scope, catalytic monoliths were prepared with the procedure presented in chapter 2, and characterized as explained in chapter 2.4 (*Characterization Techniques*). The monoliths used for the preparation of the catalysts, are 900 cpsi honeycomb monoliths, composed either by simple ceramic cordierite supports, or prepared with cordierite coated by Al_2O_3 layer. Three different nickel loading amount were used, respectively, 3w%, 5w% and above all 10w%.

The study of the activity of these materials, concerning the conversion of methane and the production of syngas, through steam reforming, partial oxidation and auto thermal reforming reaction, is related to the development of accurate, precise and reliable simulation schemes and mechanisms [29].

4.2.1. Steam reforming of methane:

Within the catalytic steam reforming reaction, the nickel catalysts are normally used, according to their high availability and low cost, compared to the other noble metal materials, such as rhodium and platinum catalysts.

For this research, such as for the previous experiments with gas-phase reaction, nickel catalysts with a support of γ -alumina are used.

The analysis of previous literature [22] gives the possibility, through a precise characterization of the materials, concerning BET analyses, TPR experiments, and hydrogen pulse chemisorption, to see that the catalyst supported by γ -alumina presents higher values of surface area (between 180 and 240 m²/g, varying with the nickel content), compared with other crystalline support forms (α - and θ -alumina).

The next catalytic results are compared both with the homogeneous reactions experiments, obtained and presented in chapter 4.1, and with the simulations of the pure gas-phase conditions.

In addition, in order to deepen the knowledge about the Ni catalyst behaviour and to better understand the values here found, the performances of the nickel metal loaded catalysts, can be also compared with the data of rhodium catalysts activity, obtained by previous works [21], and already presented in chapter 4.1.

Studying how the reaction conditions, i.e. the variation of the composition of the reactant, or the modification of the reaction temperature trend, may influence quality and amount of the products, three experiments with increasing steam to carbon ratio are presented, and they are carried out using a 10w% nickel metal loaded catalyst supported with γ -Al₂O₃ layer.



Figure 4.16: Conversion in CH₄-SR with different S/C: comparison between catalytic and homogeneous reaction. (*Rh-catalyst data from B. Schädel, M. Duisberg, O. Deutschmann, paper in preparation*) (Rh-catalyst supported only by cordierite)

In chapter 4.1.1 was already underlined how, especially in methane steam reforming, the lack of a catalytic active material over the surface of the honeycomb monoliths, used in the reaction, was accompanied by very low performances, allowing interesting values of conversion only at very high temperatures, as reported in Fig. 4.16.

In this section, it' possible to consider the great difference of the results obtained with an active catalytic material, compared to the previous experiments. Using the 10w% nickel washcoat supported monolith, the conversion curves display very high values (60-80%) already at low temperatures, around 650-750°C, almost 200°C lower than the first temperature where the homogeneous phase begins to show some interesting results.

The conversion trend of the experiments involved with nickel catalysts, presents, in spate of the used different steam content, general similar values, especially at high temperatures.

Through the experiment carried out with a low steam to carbon ratio (i.e. S/C=2), it's possible to see how the catalyst operates at low temperatures, concerning the amount of converted methane: the activity shapes values of 20% conversion although only at 450°C, and it is characterized by higher results, with the increase of the temperature, showing values around 60% conversion at 650°C, where, in the previous experiments, the blank cordierite monoliths had quite no conversion.

The analyses show moreover a very interesting agreement between the values obtained with rhodium catalyst, and belonging to previous works [21], and the performances of the here tested nickel catalysts: that is indeed an important result in the study of catalytic material, and above all of the nickel coated monoliths, which in industrial domain, are usually used and preferred than the precious metals such as Pt and Rh.

It's interesting to see the almost perfect agreement between the rhodium experiments, carried out with a steam to carbon ratio of 4, and the tests with nickel loaded monoliths, with a ratio of water to carbon of 2: that gives an important result about the energy and reactants saving, underlining the possibility to obtain similar results but with lower steam contents.

At the same time, the experiments conducted here with higher steam contents (2.5-4), show small improvements, concerning the conversion performances, in comparison with the previous studies with rhodium [21], especially at quite low temperatures, around 400 and 600°C, where the tests carried with nickel metal, present more interesting values.

Analysing other researches [22], concerning studies over the trend of methane conversion level according to the reaction time, of a nickel θ -alumina catalyst, at approximately 750°C

and a steam to carbon ratio of 1, it is possible to see how the catalysts with nickel content between 10w% and 12w%, present a high and especially very stable methane conversion according to the reaction time.

They report the different values of methane conversion or carbon monoxide yield at 750°C by steam reforming, in relationship with the varying percent of loaded nickel on the monolith surface, underlining, as said, the better activity of the 10-12w% nickel monoliths.

In order to deepen the comparison between the catalytic experiments and the homogeneous phase tests, trying to analyse and discover if an influence and a role of the gas-phase reactions on the catalytic products distribution exist, the mole fractions of carbon monoxide and carbon dioxide, obtained with the 10w% nickel supported catalyst, and here presented in relationship with the reactor temperature, are plotted in Fig. 4.17 and compared with the other ones.





Carbon monoxide mole fractions

Figure 4.17: Mole fractions in CH₄-SR with different S/C: comparison between catalytic and homogeneous reaction.

a) carbon monoxide mole fractions

b) carbon dioxide mole fractions

The choice to plot, in the figures above, the mole fractions of the products, has the intention to check and verify the possible relation, in terms of amounts (mole fractions), comparing the blank cordierite experiments with the catalytic ones.

The purpose is to see if and how the carbon monoxide and dioxide, for example, produced and seen in the steam reforming gas-phase reaction, may influence and play a role in the catalytic process products distribution.

At a first analysis of the chart 4.28, it's possible to see how the highest values of carbon monoxide and dioxide amount by catalytic tests, appear at temperatures, where the production of the same compounds by homogeneous reaction is inexistent. For example, around 800-900°C, the carbon monoxide produced in catalytic conditions, reaches the maximum of the values, showing more than 20% mole fractions, while the same carbon monoxide, present in the homogeneous phase, reaches very lower values, around 1% mole fractions.

By the homogeneous reaction, as shown in figure 4.28 a) and b), the mole fractions distributions, especially by carbon monoxide, present interesting values (also around 20%), but only at very high temperatures, 1000-1100°C approx.

This result is in agreement with the conversion trend too: in figure 4.27, through the analysis of the different conversion data, it's possible to underline a clear shift of the activation barrier of the reactant, followed, naturally by a consequent displacement and movement of the products distributions too, as seen in figure 4.28.

Indeed in figure 4.27, by catalytic tests, the methane is converted at low temperatures, temperatures where the activity of the same methane, but in homogeneous phase conditions, is inexistent. Only around 1000-1100°C, as well for the mole fractions, the gas-phase begins to show a conversion of the feedstock.

This result means that the clear and interesting activity of the homogeneous phase, seen in the previous chapters by the experiments carried with washcoat supported monoliths, and shown in the figures here, doesn't influence the activity and, above all, the products distribution of the catalytic experiments.

4.2.2. Catalytic partial oxidation and autothermal reforming of methane:

As said at the beginning of chapter 4.2, the main goal of this research is a better comprehension of the influencing parameters, such as the reactants composition or the structural properties of the reactor, controlling the products distribution.

This analysis, about the activity of 3w% nickel catalysts, in partial oxidation reaction or auto thermal reforming, using methane feedstock, belongs to a wide research for the development of models of oxidation and steam reforming [29].

Different experiments, with varying steam to carbon ratios (0-4) and consequently varying feed gas compositions, were carried out.

The reference composition (with S/C = 2) is anyway.

Methane = **0.071**

Water = **0.143**

Oxygen = **0.036**

Argon = **0.75**

Experiments with or without the use of a coating layer of γ -Al₂O₃ on the ceramic cordierite monolith, were also performed in order to comprehend the influence of the washcoat (a high surface area structural promoter) on the catalyst activity.

Figure 4.19 and 4.18 report the results of CPO experiments with a steam to carbon ratio of 2 and a ratio of methane to oxygen of 1.3, respectively over a nickel alumina supported catalyst and for the same catalyst without the support.

Clear hysteresis phenomena both by conversion and selectivity trend, are underlined and consequently studied in the experiments.

The measured conversion and selectivity are plotted as function of the temperature, measured at the end of the reactor.

The gas space velocity, the pressure and the monolith configuration (900 cpsi monolith) are the same as those used for the steam reforming experiments.



Figure 4.18: ATR of CH₄, S/C=2, CH₄/O₂=1.3; CH₄ conversion and CO-CO₂ selectivity for a 3w% Ni catalyst – effect of the temperature; (—) increasing temperature, (- - -) decreasing temperature.



Figure 4.19: ATR of CH₄, S/C=2, CH₄/O₂=1.3; CH₄ conversion and CO-CO₂ selectivity for a 3w% Ni γ -Al₂O₃-supported catalyst – effect of the temperature; (—) increasing temperature, (- - -) decreasing temperature.

At first, the experiments were carried out with increasing temperature trend from 400°C to 800°C. The observed conversion values are very low, with a prevailing production of carbon dioxide.

Indeed, in figure 4.18, in the profile of increasing temperature, the catalytic activity of the 3w% nickel catalyst, concerning the methane conversion rate or the selectivity to carbon monoxide, is not recovered until 800°C. Around 900°C, the catalyst reaches 10% conversion methane, and at the same temperature, the carbon monoxide selectivity shows values around 30-40%, while the carbon dioxide decreases drastically.

Then the catalysts were processed with a reducing treatment in 3% hydrogen atmosphere in presence of argon, for 2-3 hours at 700°C. High temperatures of the furnace were planned.

At 1000°C the methane conversion presents values around 70-80%. At decreasing temperature, the conversion decreases too, but the values are significantly higher than those of the experiments carried out with increasing temperature.

This result underlines the presence of a clear hysteresis phenomenon (different behaviour according to the heating procedure).

Moreover, the higher conversions seen with decreasing furnace temperature, are accompanied by higher selectivities to carbon dioxide, with an enhancement of the performances of \sim 30-40%

The same experiments were performed with $Ni-\gamma-Al_2O_3$ washcoated monoliths. The results are reported in figure 4.19.

At increasing temperature, the conversion of methane was low up to 800° C, where a remarkable increase of the conversion was observed: it passes from ~10% to about 90%.

The same result was seen in the selectivity to carbon monoxide, which between 800°C and 900°C, increases from \sim 20% to \sim 60%.

A run at decreasing temperature was also performed. At starting temperature of 1100°C, the conversion amounted to 90% and the selectivity of carbon monoxide to 70%. At decreasing temperatures, the conversion of methane smoothly decreases, amounting to 50% at ~ 500°C, such as the carbon monoxide selectivity, with values around 20% at 500°C.

Analysing the carbon dioxide selectivity trend in figure 4.19, the decreasing temperature profile, compared with the increasing temperature one, presents generally a decrease of about 20%, between 500°C and 900°C.

The comparison between the results in figure 4.18 and those in 4.19, clearly shows that the presence of the washcoat greatly enhances the monolith performance. Indeed the presence of the γ -Al₂O₃ provides the necessary surface area (and thus a dispersing media for the Ni particles) which lacks in the case of the non-coated monolith.

Both with and without coating, the experiments showed the existence of an hysteric behaviour of methane conversion and consequently also in the selectivities profiles.

Such a behaviour of the Ni-catalysts is known in the literature of methane-CPO [9, 30, 31] and it was been explained based on the relative stability of oxide and reduced state of the Ni particles. For example in [30], the authors underline how these phenomena suggest that a multiple state of the nickel surface can exist. They study CPO experiments and changing the methane partial pressure in ascending and descending orders, they see a large hysteresis loop in the rate of methane oxidation and also in the selectivity towards carbon monoxide formation.

They suggest the presence of two different state of the catalyst surface: an "oxidized" state, active for combustion of methane to carbon dioxide, and, by very high methane partial pressure, a "reduced" state, more active and selective to carbon monoxide.

The oxide state is stable at lower temperature and a threshold temperature exists, at which metallic Ni particles tend to form.

When the reduction process initiate, since the metal particles are active for the reforming of methane, then syngas is formed, which, for its intrinsic composition, enforces the reducing force of the gas-phase environment. This fact promotes the complete surface reduction.

As shown in figure 4.19, at increasing temperature a lower conversion characterizes the process, until the reaching of a characteristic temperature (threshold temperature), at which the conversion has a dramatic increase.

On the opposite, as shown in both the figures, 4.18-4.19 (that means with both the monolith surface configurations), when starting the experiments from high temperature, the surface is in the favoured reduced state (due both to the temperature and also to the reducing atmosphere) which is kept also at decreasing temperature, since the surface chemistry contrasts the adsorption of oxygen molecules on the monolith surface, and consequently the formation of NiO_x species. That could explain the clear hysteresis phenomena seen in the analyses above.

Quite similar are the results obtained in [9], where a close examination of the activity of nickel catalysts by oxidative steam reforming of methane, accompanied by a careful characterization of the same catalysts, is presented. They present a clear and severe hysteresis effect in methane conversion and carbon monoxide selectivity, with respect to decreasing and increasing temperature, using a composition of methane/steam/oxygen/argon = 40/30/20/10 and a pure nickel catalyst supported by aluminium oxide. Trying to explain the very low activity of this catalyst, at temperatures lower than 650° C, and the higher activity, by the decreasing temperature profile, of the same catalyst, they consider these hysteresis phenomena as a consequence of a reduction process of the oxidized Ni species, in presence of reducing agents like methane, carbon monoxide and hydrogen (syngas).

In order to better show the effect of the washcoat presence, anyway already seen in the comparison of figures 4.18 and 4.19, the trends in methane conversion and carbon oxide compounds , in the profile of decreasing temperature, with the same operative conditions, are here below repeated.



Figure 4.20: ATR of CH₄, S/C=2, CH₄/O₂=1.3; CH₄ conversion, CO-CO₂ selectivity for a 3w% Ni catalyst, (- - -) decreasing temperature profile. Comparison of the washcoat effect.

In figure 4.20 **a**), around 1000-1100°C, the conversion rate of the no-supported catalyst shows values around 70-80%, and, with decreasing temperature, falls of drastically until 10% by 700°C. The supported catalyst shows, on the contrary, a different trend of the values, which, with decreasing temperature, slowly decreases, maintaining values around 80-90% of conversion for a large temperature range, between 750-1000°C.

Similar is also the behaviour of the two catalyst configurations, by carbon monoxide selectivity, in figure 4.20 b).

By carbon dioxide selectivity (figure 4.20 c)), with decreasing temperature, the catalyst without the alumina support, increases drastically from 30% at 1050°C to 100% at 800°C. As seen before for conversion and carbon monoxide, the supported catalyst presents a milder and, in this case, lower increase of the values, reaching 80% selectivity only around 500°C.

As seen before, and as underlined in literature, the nickel surface can be easily oxidized to NiO species, and it's difficult to maintain the reduced Ni configuration in oxygen atmosphere. The enhancement in the performances, seen in figures 4.20, through the use of an alumina supported catalyst, can be sought in the higher accessibility of the Ni particles on the aluminium oxide surface. The effect, obtained with the washcoat presence, is an apparent enhancement of the Ni load.

This effect could be better inspected and understood through detailed analyses of characterization of the surface, in order to collect more data over the Ni dispersion.

Also for the hysteresis, the knowledge of the surface conditions or alterations regulating these phenomena is still too low. Interesting would be the consolidation of the knowledge through successive analyses of the surface of the catalysts after the use in the reactor, by XRD or temperature-programmed reductions.
5. Conclusions

Previous studies about the CPO and SR activity of Rh coated honeycomb reactors were extended with an analysis of the possible non-catalytic contributions to the process chemistry, and with additional experiments with noble metal free Ni/γ -Al₂O₃ coated monolith.

The homogeneous gas-phase steam reforming experiments, as seen in the previous pages, were conducted with light hydrocarbons, namely methane, ethane and propane, in the presence of honeycomb monolith.

The operating conditions reproduced those of previous catalytic experiments.

The investigated parameters were: the steam feed content and the presence of a γ -Al₂O₃ layer.

• <u>Methane</u>: the most unexpected result was found in the methane gas-phase experiments. Indeed, the measured amount of converted methane exceeded that predicted on the basis of the gas-phase chemistry. Higher conversions and higher carbon monoxide yields, than those of a purely homogeneous reactor, were observed at temperatures of 1000-1100°C.

While the literature tends to exclude the possible effects of radical seeding on the monolith wall with a promotion of gas-phase chemistry, this result can be interpreted by assuming that the porous aluminium oxide layer exerted an "heterogeneous wall effect", possibly related to the presence of metallic impurities with some SR activity at the very high temperatures of the experiments.

• <u>Ethane/Propane</u>: the most important result obtained in the ethane/propane analyses was the very appreciable agreement between the experimental results and the predictions of purely gas-phase reactor. In the products distribution, comparing the simulations and the experiments, only light and small differences were observed, with enhancement or decrease of some products.

Likely the presence of the washcoat surface produced a light "quench effect" of the radical reactions, with for example, an enhancement in methane selectivity and a decrease in ethane one, observed in the propane experiments.

Ni-coated honeycomb catalysts were then prepared and tested. 10w%-Ni washcoated catalysts were tested in the methane steam reforming reaction and the results were compared with the performances seen in the gas-phase tests: the comparison showed that the residual activity of the washcoated monoliths doesn't influence the products distribution of the catalytic experiments, wherein the methane is activated at much lower temperature.

3w%-Ni coated catalysts were instead tested in CPO experiments, with a steam to carbon ratio of 2 and a ratio of methane to oxygen of 1.3, in order to study the influence on the activity of the presence of the washcoat layer too.

The comparison clearly showed that the presence of the washcoat greatly enhances the monolith performances. Both with and without γ -Al₂O₃-coating, the experiments showed the existence of hysteretic behaviours in terms of conversion and selectivities trends vs. temperature. Experiments started at high temperatures showed indeed very higher performances, and that was interpreted as a result of the high-reduced state of the catalyst surface, favoured both by the high operating temperatures and the reducing atmosphere. This high-reduced state seems to contrast the adsorption of oxygen and the consequently formation of NiO_x species on the surface, which are on the opposite favoured when the experiments start at low temperature.

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