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Catalytic decomposition of methane -Experiments with metal catalysts



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Abstract

Pre-combustion carbon capturing method “Thermo-catalytic decomposition of methane” has been studied at Tampere University of Technology (TUT) as a part of the Carbon Capture and Storage (CCSP) program coordinated by CLEEN Ltd. The previous research of methane decomposition is continued by experiments with metal catalysts.

In the literature, the research of the catalytic decomposition of methane (CDM) is focused much on nickel catalysts. The product carbon properties are dependent on the possibly used catalyst. The following carbons have been found in CDM process: carbon nanotubes, carbon nanofibers, graphene, and graphite. Drawbacks in CDM with metal catalysts are the deactivation of the metal catalysts due the product carbon formation and the possible purification of the product carbon depending on its utilization.

At TUT the experimental study of CDM was carried out in a ceramic reactor with four porous metal catalysts. The methane volumetric flow was constant, i.e., 150 ml min^{-1} , and the experimented reaction temperatures were between 300 and 1000 °C. According to the results, catalysts 2 (Rh+ZrO_x) and 4 (Ir) did not promote the methane decomposition reaction. With catalyst 3 (ZrO_x), methane decomposition was observed at 800 °C, but the methane conversion was no more than around 5 % and the catalyst deactivated in less than two hours. In the experiments with the same setup the thermal methane decomposition without a catalyst began at temperatures above 900 °C.

Catalyst 1 (Ni) showed the most interesting results. With Ni-catalyst the methane decomposition was observed at temperatures of 500-700 °C. The highest observed instantaneous methane conversion was 40 %. A drawback of the Ni-catalyst was that the produced carbon broke down the catalyst pellets. However, at temperatures of 500 and 550 °C the methane conversion of 10-17 % was measured to last up to 400 min.

The results indicated the possibility of autocatalytic effects in the methane decomposition reaction, i.e., the product carbon catalyzed the reaction. The catalyst pellet breakdown and part of the long catalytic activity can be explained with the production of whisker carbon. Whisker carbon, also called as filamentous carbon, is carbon nanotubes and nanofibers, which have a metal particle in the tip of each carbon filament. In CDM these metal particles could be able to decompose more methane and increase the length of the carbon filaments.

The results with nickel catalyst were promising. Therefore, further research around CDM should focus at least on nickel catalyst.

ACKNOWLEDGEMENT

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ABBREVIATIONS AND SYMBOLS

Abbreviations

AC	Activated carbon
ATP	Autothermal pyrolysis
CB	Carbon black
CCS	Carbon capture and storage
CDM	Catalytic decomposition of methane
EDS	Energy-dispersive detector
FP	Funding period
FTIR	Fourier transform infrared
ID	Inner diameter
MSI	Metal support interaction
OD	Outer diameter
SEM	Scanning electron microscope
STP	Standard temperature and pressure
TDM	Thermal decomposition of methane

Symbols

ΔH_r^0	J mol^{-1}	reaction enthalpy at STP conditions
\dot{n}	mol s^{-1}	molar flow
t	s	time
M	g mol^{-1}	molar mass
m	g	mass

Chemical elements

Al	Aluminum	O	Oxygen
C	Carbon	Pd	Palladium
Co	Cobalt	Pt	Platinum
Cu	Copper	Rh	Rhodium
Fe	Iron	Re	Rhenium
H	Hydrogen	Ru	Ruthenium
Ir	Iridium	Si	Silicon
Mg	Magnesium	Ti	Titanium
N	Nitrogen	W	Wolfram
Nb	Niobium	Zr	Zirconium
Ni	Nickel		



1 INTRODUCTION

The EU climate and energy package has set a target to each EU member country to decrease greenhouse emissions and energy consumption as well as increase the use of renewable energy according to the 20-20-20 –target. An essential method to reduce the greenhouse emissions is the CO₂ emissions trading. However, at the year 2013 the price of emission allowances has been 2.5–7 €/t CO₂ [1] and the objective is to raise this price to get the emission trading system to work as it was originally planned. Carbon capture and storage (CCS) technology is providing one option to control the emissions, but at the current market price of emission allowances the technology is not economically feasible. According to the calculations done at VTT, 10–30 % of the greenhouse emissions in Finland at the year 2050 could be captured provided that the emission allowance price is 70–90 €/t CO₂ [2].

At the year 2012, 8 % of the total energy consumption in Finland was produced with natural gas [3]. The thermal decomposition of methane (TDM) technology could provide a transitional period solution to cost effectively continue natural gas usage before the CCS-system is completely developed. In TDM reaction the methane in natural gas (over 98 %) is thermally decomposed to produce gaseous hydrogen, solid carbon, and minor amounts of higher hydrocarbons. The energy required in this endothermic reaction can be also produced by partly burning the methane (a process called autothermal pyrolysis, ATP). The reaction temperature can be decreased by using catalysts. The chemical composition of the produced solid carbon depends on the reaction conditions and the possibly used catalyst. The economic value of the carbon products is varying; in the previous studies higher value products such as carbon nanotubes [4] and carbon black [5] have been found.

The hydrogen produced in the TDM process is also an interesting product as only in the USA over 10 million tons of hydrogen was produced during the year 2006 [6]. The most significant hydrogen consumers are oil refining, food industry, and chemical industry. Currently the hydrogen is produced mainly by steam reformation of natural gas, e.g., in the USA 95 % of the total produced hydrogen [7]. Main drawback of the steam reformation technology is the produced carbon dioxide emissions. As the TDM process tackles the carbon dioxide emissions, it has possibilities to become an alternative method in hydrogen production provided that the overall economic cost of TDM is competitive compared to the steam reforming.

The TDM process has been researched at TUT as a part of the Carbon Capture and Storage Program (CCSP) coordinated by CLEEN Ltd from the beginning of the program at 2011. During the first funding period (FP I) a literature survey and first laboratory experiments were conducted. In the experimental part thermal methane decomposition and preliminary catalytic reaction conditions were studied. Further research was needed to maximize the methane conversion percentage by optimizing the process parameters and finding a suitable catalyst. It

was admitted that producing hydrogen with TDM would be feasible only if it can compete economically with the current technology, steam methane reformation.

During the FP II, the focus of the experiments was to find a suitable and preferably cheap and abundant catalyst for reaction. Therefore, the catalytic effect of quartz sand and biomass-based char were studied. However, those had a negligible effect on the methane conversion rate, and furthermore, bio char lost completely its active surface area probably due melting of the ash components. The conclusion was that high catalyst surface area is a critical requirement in order to reach even a moderate decomposition rate. Further research was suggested to be experiments with metal catalysts.

Wide experimental research was conducted during FP III. Extensive tests of TDM were conducted to study the effect of reaction temperature and methane volumetric flow (i.e. residence time) on methane decomposition. An alternative method to produce the heat needed in methane decomposition, autothermal pyrolysis (ATP), was tested also. The experimental results of these studies will be published in the Master's Thesis "Thermal decomposition and autothermal pyrolysis of methane" by Jaana Rajamäki (TUT) at spring 2014. A literature survey about possible carbon morphologies produced in methane decomposition and a market analysis of these products have been conducted at TUT by Katariina Tolvanen. The results are presented in the report "Thermo-catalytic decomposition of methane –carbon product utilization and market analysis". The test results of catalytic decomposition of methane (CDM) conducted with the metal catalysts are presented in this report.

2 THEORETICAL BACKGROUND

In the literature, the studies related to methane decomposition are mainly focusing either on the hydrogen production, product carbon properties or development of new catalysts. This theoretical background presents the use of both metal and carbon catalysts in methane decomposition process. Nevertheless, the focus is primarily on metal catalysts as those are studied in the experimental part. Research results presented in the literature about the autocatalytic effects, i.e., the carbon product of catalytic methane decomposition serving as a catalyst for the reaction, are presented also. The autocatalysis could tackle one of the main problems in the use of catalysts, deactivation due to the carbon deposition on the original catalyst.

2.1 Hydrogen production

The endothermic reaction of methane decomposition (also called as methane decarburation and (direct) methane cracking) is described with the following reaction equation [8]:



In practice, the reaction products are solid carbon, gaseous hydrogen, and higher hydrocarbons. The methane conversion and produced carbon properties depend on the reaction conditions, e.g., temperature, and the properties of the possibly used catalyst.

The equilibrium curve (Figure 2.1) presents the theoretical maximum methane conversion that can be achieved at a certain temperature.

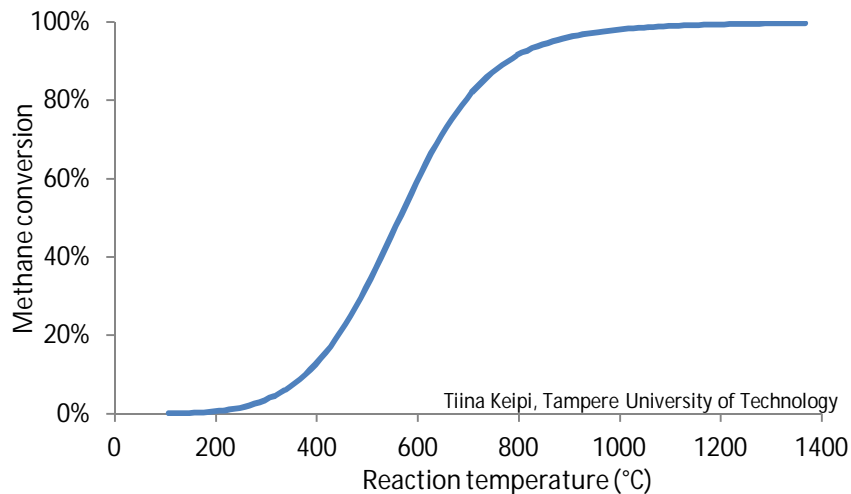


Figure 2.1. The equilibrium curve for methane decomposition reaction.

The equilibrium curve does not reveal the time required to achieve the equilibrium. In the experiments conducted in our ceramic reactor at TUT, the TDM reaction began at temperatures around 900 °C and at 1200 °C conversions above 90 % were achieved.

Currently, the most used method to produce hydrogen is the steam reforming of natural gas, which can be described with the following two-step reaction equation:

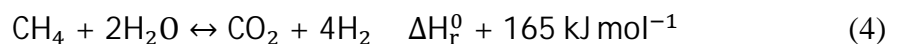
Reforming reaction:



Water gas shift reaction:



The overall reaction:



When hydrogen is produced with TDM, the energy requirement is 37.8 kJ mol⁻¹ H₂, which is significantly lower compared to the steam reforming (63.3 kJ mol⁻¹ H₂). Furthermore, steam reforming produces CO₂ that is more complicate to sequester from the atmosphere than the solid carbon from the methane decomposition process. [9]

2.2 Catalytic methane decomposition (CDM)

The methane decomposition reaction can be catalyzed to decrease the reaction temperature. The produced carbon properties are dependent on the nature of catalyst material. The catalysts used in the catalytic methane decomposition (CDM) process are divided into two groups,

metal and carbon catalysts. Generally, when catalysts are used in processes such as natural gas steam reforming or refining of biomass gasification gas, the target is to achieve a longer catalyst activity by preventing the formation of solid carbon.

2.2.1 Metal catalysts

Generally, the catalytic activity of transition metals has been stated to follow the descending order: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe [10]. The selection of an appropriate support material is greatly influencing to the properties of the metal catalyst. The most important factors are the metallic catalyst particle size and the dispersion and stabilization on the surface of support material. [11] A drawback of the use of metal catalysts is that the produced carbon often has to be purified from the metal particles in the carbon [12].

Nickel is a widely studied and generally found as suitable catalyst material for CDM [11], [13], [14], and [15]. Methane decomposition has been detected as low temperatures as 200 °C in the presence of Ni-catalyst [16]. The optimal reaction temperature of Ni catalyst in CDM is around 550-600 °C. Total deactivation at different temperatures above the optimal has been reported. [11]

In the CDM study with a commercial Ni-catalyst (Ni content 65 wt-%, supported on a mixture of silica and alumina) Suelves et al. [17] achieved in fixed-bed reactor methane conversions near to the thermodynamic equilibrium. The methane conversions were around 30 % at 550 °C, 55 % at 650 °C, and 65 % at 700 °C, when the corresponding thermodynamic equilibrium values are 40 %, 70 %, and 80 %, respectively. These results were achieved with fine catalyst particles with particle size less than 100 µm. The fresh catalyst contained NiO, and therefore, a reduction treatment in hydrogen flow was conducted before all the experiments.

The nickel concentration in the catalyst affects to the catalyst activity. Ermakova et al. [18] achieved the highest carbon yield with nickel concentration of 90-96 %. On the other hand, Venugopal et al. [15] have found 30 wt-% nickel on SiO₂ support at a temperature of 600 °C as the optimal concentration for CDM producing the highest amount of hydrogen and carbon nanofibers. The catalyst preparation methods have been different in these studies.

According to the study of Echegoyen et al. [19], adding a small amount of copper to a nickel/alumina catalyst during the catalyst preparation resulted in an increased hydrogen yield and better catalyst stability in CDM. Similar results have presented also [20] and [21].

Besides nickel, the metal catalysts studied in the experimental part of this work are not commonly presented in the literature. In a study of CDM over iridium catalyst, methane decomposition has been observed as low temperatures as 200 °C. At higher temperatures the extent of the decomposition increased and was 2.0-5.0 % at 500 °C. However, the conversion was rather low and the catalyst deactivated rapidly. [22]



2.2.1.1 Metal catalyst support material

Both the catalyst support and the active metal have an influence on the CDM reaction. Therefore, studies of different catalyst support materials especially for Ni catalysts have been reported. The support material may affect the deposited carbon morphology. Furthermore the surface oxygen in the support may react with the deposited carbon and change the outlet gas composition by producing carbon monoxide. [15] and [23]

In many studies SiO_2 have shown the highest activities and longest lifetimes [18] and [24]. Li et al. [21] studied the effect of niobium oxide (Nb_2O_5) as a support for catalyst in CDM. One of the highest amounts of deposited carbon presented in the literature, 743 g C per g of Ni, and 7274 mol H_2 per mol Ni was measured at 600 °C when NiCu-catalyst (50.8 wt-% and 21.2 wt-%, respectively) was supplied with Nb_2O_5 support material (catalyst molar ratios 65Ni-25Cu-5 Nb_2O_5).

2.2.1.2 Metal catalyst preparation

The studies focusing on the effect of catalyst properties on CDM are mainly conducted with self-made catalysts. According to the literature survey done by [11] the most used catalyst preparation methods are impregnation and co-precipitation. In the impregnation process the catalyst metal is dissolved in water or other solvent and contacted with the catalyst support material which absorbs the catalyst metal. In the co-precipitation the catalyst metal is precipitated together with the support material. The main drawback is that the both processes require huge amounts of water because of catalyst washing and filtering. Generally, in the catalysts prepared by impregnation or precipitation the interaction between metal and support is weak and the metal loading of the catalyst is low (below 20 wt-%). [11] and [25]

According to [11], the solid catalysts were typically crushed and ground prior to the experiments. In the same survey, the catalyst particle size varied from several dozen μm to several mm. The catalysts surface areas varied between 6 and 786 $\text{m}^2 \text{g}^{-1}$. The selection of catalyst form and particle size is highly dependent on the experimental setup.

2.2.1.3 Metal catalyst pretreatment

After the catalyst preparation, the catalyst needs to be activated by calcination and reduction steps. The calcination treatment removes the residual precursor species and changes the precursor material to metal oxide. The reduction step transforms the metal oxides to the active metal phase. [23]

Qian et al. [26] have studied the effect of catalyst reduction treatment on the methane decomposition reaction. The two tested metal catalysts were Co/Mo/ Al_2O_3 and Ni/Cu/ Al_2O_3 catalysts with weight ratios of 1/4/50 (Co/Mo/Al) and 15/3/2 (Ni/Cu/Al), respectively. The methane decomposition experiments were conducted at 823-1123 K both with unreduced catalysts and catalysts reduced by hydrogen (973 K, 3 h). The methane conversion and the carbon nanotube production were higher with both unreduced catalysts.

According to the explanation given, the simultaneous catalyst reduction may provide the energy required in the endothermic methane decomposition reaction. As part of the hydrogen and carbon are consumed when oxidizing them to H₂O and CO, the methane decomposition equilibrium shifts towards the direction of hydrogen and carbon nanotubes production. Using reduced or unreduced catalysts did not show any obvious difference in the morphology of carbon nanotubes, and the CO concentration was very low in the hydrogen produced with unreduced catalyst.

2.2.1.4 Product carbon form with metal catalysts

A few different type of carbon products have been observed in CDM with metal catalysts. Nickel-catalyzed CDM at a temperature of 700 °C produced highly ordered graphite [17]. In the study of Fenelonov et al. [27] methane was decomposed over Ni and NiCu catalysts at 550 °C and the carbon product was graphene. In many studies the product is filamentous carbon, the formation of which is presented more detailed in the following chapter.

2.2.1.5 Whisker carbon formation

Filamentous (whisker) carbon is a deposit structure containing carbon and metal particles and the term refers to the following carbon allotropes: carbon nanotubes, carbon nanofibers, and microcoils [28]. Suelves et al. [29] tested NiCuAl catalyst at 700 °C and produced filamentous carbon. Wang et al. [30] observed 600 °C as an optimum temperature for the formation of filamentous carbons with Ni-catalyst. In the study of Awadallah et al. [31] bimetallic catalysts NiFe, NiCo, and FeCo at a temperature of 700 °C promoted the formation of carbon nanotubes. The Fe-containing catalysts were observed to produce also carbon nanofibres.

The CDM study of Guil-Lopez et al. [32] was conducted with a thermogravimetry at temperatures of 950-1000 °C. All the metal catalysts, i.e., six different Ni-catalyst and two iron oxide catalysts, produced carbon nanotubes and carbon nanofibers.

At temperatures below 600 °C the methane decomposition with metal catalysts promoted the production of whisker carbon. Whisker carbon has two growth mechanisms: base growth and tip growth (shown in Figure 2.2). The catalyst material is an important factor as the growth mechanism depends on the metal support interaction (MSI). When the interaction between the metal and support is strong, the metal particles stay on the catalyst surface and the carbon filaments grow on a metal particle (base growth). With a weaker interaction, the metal particle detaches from the catalyst surface and moves to the tip of the formed carbon filament (tip growth). The former mechanism destroys the catalyst. [25] [33]

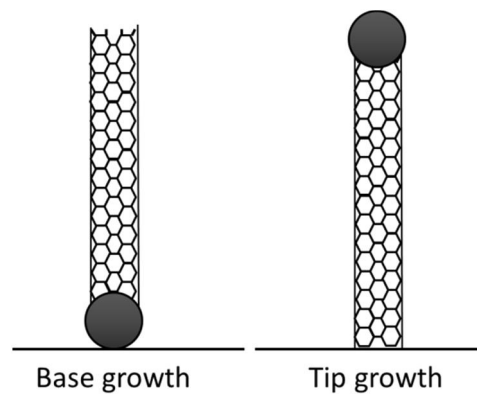


Figure 2.2. A schematic of the whisker carbon formation mechanisms.

Takenaka et al. [34] have studied the filamentous carbon formation in the decomposition of methane over Ni catalyst. They reported that a Ni metal particle was fastened on the tip of the each formed carbon filament. According to the given explanation these Ni metal particles stay active and are able to decompose more methane and increase the length of the carbon filaments.

2.2.2 Carbon catalysts

Carbonaceous materials in CDM are considered appealing because of few reasons. Carbonaceous catalysts have lower cost than metallic ones [35], there is no need for the carbon separation from the catalyst surface [8], the carbon produced during the reaction could be suitable as catalyst after activation [35], and the reaction could become autocatalytic if the produced carbon properties could be modified to catalytically active [36].

Generally, the most important catalyst properties are the chemical composition, surface area, porosity, pore-size distribution, stability, and mechanical properties. Most studies of carbonaceous catalysts in CDM have focused on activated carbon (AC) and carbon black (CB) because of their activity and good stability. ACs are manufactured from different carbon-based sources and this source together with the manufacturing process affects greatly to its catalyst properties [11]. According to [37], the amount of accumulated carbon from methane decomposition on AC catalyst surface is only a fraction of the theoretical value, i.e., the total pore volume of catalyst. Thus, the AC accumulation capacity is dependent both on porosity and pore-distribution.

Different commercial CBs have been used in CDM experiments. Similarly with ACs, the origin of CB defines its properties [11]. AC and CB have a different deactivation behavior. According to [38], ACs have a high reaction rate at short time but those deactivate completely after longer reaction times. On the contrary, CBs are both initially reactive and have a good resistance to deactivation.

In the study of Suelves et al. [39] the deactivation of five commercial CBs and one AC were compared. The catalyst was stabilized by pretreating it under a nitrogen flow. The highest deposited carbon amount, 6.13 g carbon deposited per g catalyst, showed CB BP2000.

However, carbon deposition on catalyst surface in CDM deactivates the catalyst relatively fast, and therefore, regeneration is necessary.

2.2.2.1 Carbon catalyst properties

The CDM studies with carbonaceous catalysts are typically conducted with commercial catalysts. The most important carbon catalyst properties are the chemical composition, surface area, porosity, pore-size distribution, stability, and mechanical properties. According to the literature survey [11], the carbon catalyst surface area varied in a wide range between 0.54 and 3370 m² g⁻¹. The largest surface areas occurred typically in activated carbons. The mean particle size was reported to vary between a few nm and several mm. [11]

2.2.2.2 Product carbon form with carbon catalysts

In the study of Zhang et al. [12], the CDM with carbon catalyst produced both fibrous and amorphous carbon at a temperature of 850 °C. Guil-Lopez et al. [32] have experimentally studied the CDM with thermogravimetry at reactor temperatures of 950-1100 °C. The product carbon morphology depended on the catalyst material as follows: (i) activated carbon as catalyst produced carbon black, (ii) carbon black catalyst produced amorphous carbon, and (iii) with carbon nanotubes the produced carbon deposited on the original catalyst in a form of carbon nanotubes.

2.3 Autocatalytic effects in CDM

Autocatalysis in methane decomposition, i.e., the product carbon acting as the reaction catalyst, is a tempting possibility and it is frequently mentioned in the literature, e.g., [39] and [40]. A life cycle assessment [41] have been done to compare the environmental impacts and CO₂ emissions of different hydrogen production technologies, i.e., thermal and autocatalytic methane decomposition and steam reforming both with and without CO₂ capture and storage. According to the study, the autocatalytic decomposition with a 100 % conversion was the most environmentally-friendly process. Even with a 50 % conversion the autocatalytic decomposition was environmentally better option than the steam reforming. When comparing with the TDM, the autocatalytic decomposition had a slightly higher environmental impact but lower energy consumption. Despite the interesting features, only few publications have been made about the autocatalytic effects in methane decomposition process.

Chen et al. [42] published as early as 1976 a journal article about the autocatalytic effects in the decomposition of methane. The autocatalytic effect was clearly observed in the study. However, neither the carbon deposition on reactor surface nor smoke-like suspension of carbon particles in reactor was detected to be the reason for the autocatalytic reactions.

Serrano et al. [43] have studied the autocatalytic effect of the carbon produced in CDM. Different types of carbonaceous catalysts were used: two mesoporous carbons and two commercial CBs. The experiments were conducted with simultaneous Differential Scanning Calorimetry and Thermogravimetric Analyzer (DSC-TGA) at atmospheric pressure and at a



temperature range of 890–990 °C. After the initial catalyst deactivation, autocatalytic effects of the deposited carbon were observed. However, after a short period of increasing the carbon deposition rate, the formed active sites deactivated. Especially in mesoporous carbon this deactivation was not complete as a constant carbon production was observed even after 48 h when 24 g of carbon per g of initial catalyst was formed.

Lee et al. [44] studied the CDM over five CB catalysts at temperatures between 850 and 1050 °C. After the original catalyst deactivation, a period of increasing conversion was detected especially at temperatures above 1000 °C. The authors explained this behavior with the catalytic activity of the deposited carbon.

According to Zhang et al. [12] the CDM with carbon catalyst produced fibrous carbon that was active and catalyzed further the methane decomposition. In the study, the methane conversion increased along with the amount of formed carbon. After 10 h the methane conversion increased from 27 % to 61 % and more than 36 g carbon per g of raw catalyst was produced.

3 METHODS AND MATERIALS

The experiments were conducted in the laboratory of the Department of Chemistry and Bioengineering at TUT. This chapter presents the experimental setup, used catalysts, and the procedure to conduct the experiments.

3.1 Test rig

The experimental system shown in Figure 3.1 is a modified version of the setup used in FP II. The previous stainless steel reaction vessel was changed to a ceramic tube (Anderman Industrial Ceramics, UK), because of the better thermal stability and non-catalytic activity of the latter. The ceramic tube (ID 25 mm) was partly inside an electrically heated oven. The reactor temperature was automatically controlled by a thermocouple measuring the temperature inside the ceramic tube.

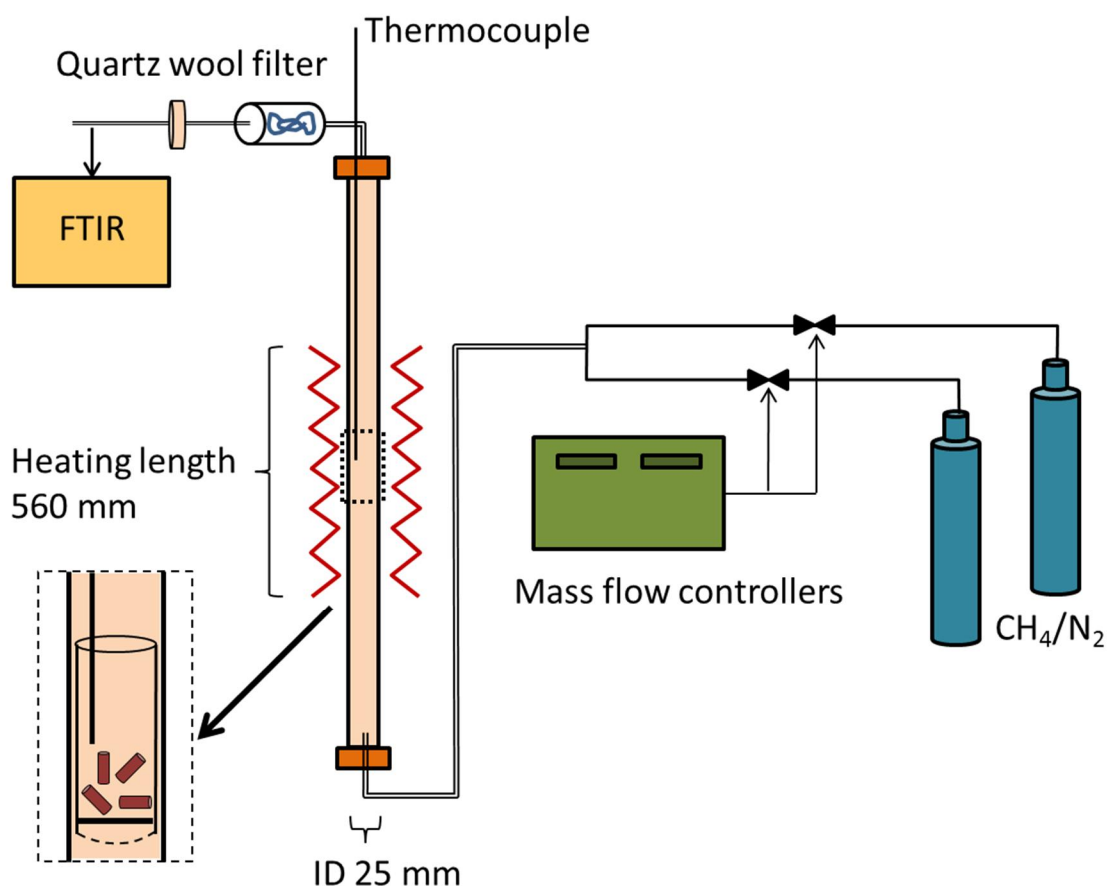


Figure 3.1. The test rig for the methane decomposition experiments.

The Bronkhorst mass flow controllers were used to adjust the gas flow to the reactor. The gas flow direction in the reactor was upwards, the selection which was done already at the beginning of the FP I. The reaction product gas was mixed with gaseous nitrogen flow of 4.5 l min^{-1} to ensure that FTIR (Fourier transform infrared analyzer) has the required volumetric flow, i.e., at least 4 l min^{-1} .

The main difference compared to the previous setup was the improving of the filtering system. The previous piece of quartz wool placed inside the reactor was replaced with a filter system containing more quartz wool outside of the reactor. The new filter system works also as a separating chamber for the carbon particles.

Two different setups shown in Figure 3.2 were used to contain the catalyst pellets/grains: a ceramic container (material Alsint 99,7; size $22 \times 17 \times 100 \text{ mm}$, ODxIDxL) produced by MTC Haldenwanger and a self-made basket made of Kanthal resistance wire (diameter 0.5 mm). Both containers are shown in Figure 3.2.

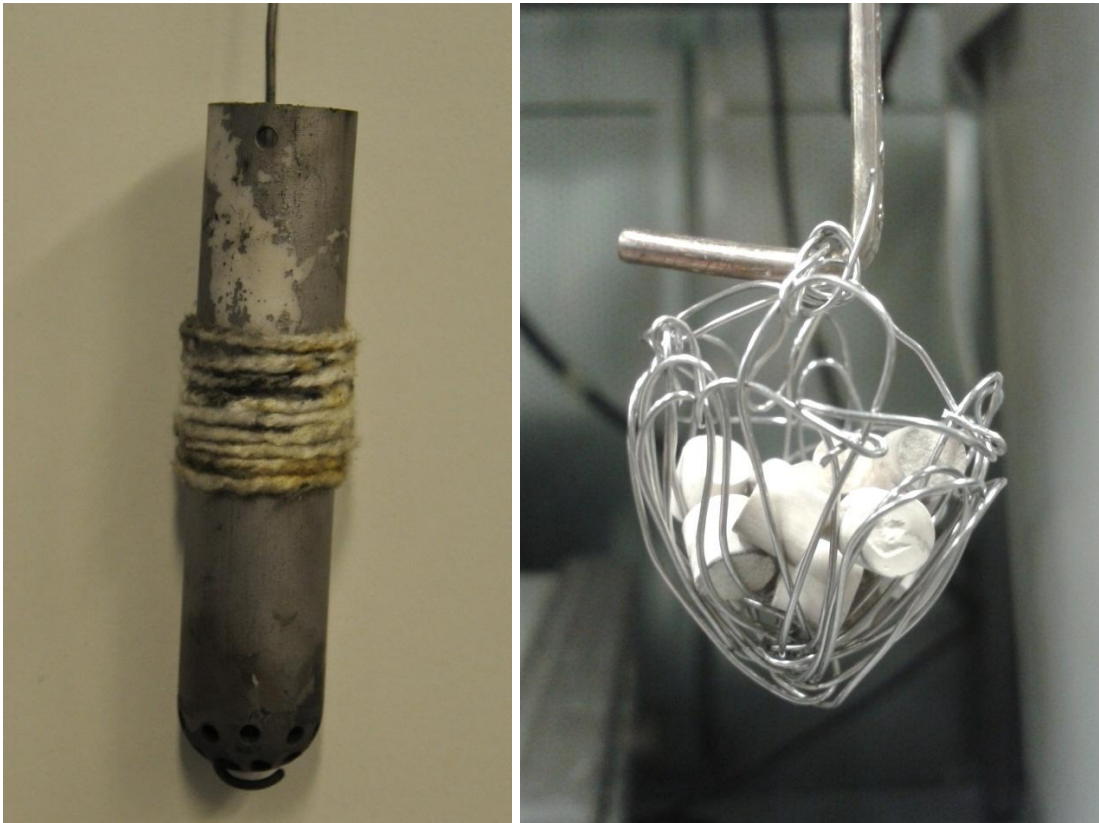


Figure 3.2. The catalyst pellet containers: the ceramic container on the left and the basket made of resistance wire on the right. Diameter of the both containers was close to the inner diameter of the reactor, i.e., 25 mm.

Bottom of the ceramic container was drilled full with small holes to enable methane flow through the catalyst bed. A kaowool grate was placed to the bottom of the ceramic container to carry the catalyst bed. Around the container was coiled a heat-resisting woolen band to prevent the methane flow between the container and reactor walls. With the container it was possible to hold the catalyst at the hottest spot in the reactor, i.e., in the middle of the heated part of the reactor, as shown in Figure 3.1.

Both catalyst containers were hanging by a thermocouple inside the reactor. The thermocouple was a natural choice because there was already one thermocouple controlling the oven temperature. Therefore, additional possibly catalytic materials were avoided inside the reactor.

With catalyst 1 neither of these containers was needed as the pellets were hanging by a bare thermocouple in the middle of the reactor. Therefore, all additional materials were avoided in the experiments with this catalyst.

Tests conducted without catalysts showed that the Kanthal-basket had some catalytic effect on methane decomposition at temperatures above 900 °C. Furthermore, the solid carbon product had a visibly different structure, i.e., more metallic-like than with the ceramic container or empty reactor.

3.2 Materials

The decomposition experiments were conducted with high purity methane (99.995 %) and the reaction products were diluted with nitrogen before FTIR-analysis.

3.2.1 Catalysts

The catalyst samples were supplied by Neste Oil. The catalyst samples and the total amount of those were:

- Sample 1: Nickel with thermally durable carrier (shaped), the total amount: 20 g
- Sample 2: Rhodium with zirconium oxide (pellet), the total amount: 20 g
- Sample 3: Zirconium oxide (pellet), the total amount: 55 g
- Sample 4: Iridium with acid, thermally durable carrier (grain size 0.15-0.35 mm), the total amount: 5 g

The catalysts needed no further processing and those were used as such in the experiments.

3.2.2 The apparent surface areas of the catalysts

The apparent surface areas of the catalysts were defined and those were used to compare the catalysts. Comparing the catalysts with different size and shape is more convenient by using the surface area as a meter instead of catalyst mass.

Table 3.1. *The catalyst properties. Diameter, length, and reactive surface refer to the average dimensions of a single catalyst pellet/grain.*

Catalyst	Material	Form	Diameter (mm)	Length (mm)	Reactive surface (mm ²)	Total mass (g)
1	Nickel with thermally durable carrier	shaped	13.1	16.9	1630	20
2	Rhodium with zirconium oxide	pellet	4.8	4.5	100	20
3	Zirconium oxide	pellet	3.3	7.2	90	55
4	Iridium with acid, thermally durable carrier	grain	0.15-0.35	-	0.2	5

In this study, the catalysts' apparent surface areas are proportional to the surface area of catalyst 1. Thus, 16 pellets of catalyst 2 and 18 pellets of catalyst 3 are equivalent to 1 pellet of catalyst 1, i.e., the relative surface area: 1. Due to the small grain size of catalyst 4, the same method was not applied to it.



3.3 Experimental arrangement

The influence of the process parameters to the activity of the catalysts were not studied comprehensively. Instead, the aim was to study the activity and deactivation of the catalysts with selected process parameters. Furthermore, due to the limited amount of catalysts it was not possible to conduct repetitive experiments with all runs to increase the reliability. Nevertheless, some repetitions were done.

All the experiments were conducted with pure methane volumetric flow of 150 ml min^{-1} . Catalyst 1 pellets were hanging by a thermocouple in the middle of the reactor and catalysts 3 and 4 were in the ceramic container. In the experiments with catalyst 2 both the ceramic container and Kanthal-basket have been applied; the used setup is marked in the experimental results.

During the first experiments, leakage tests of the cold reactor were conducted at the beginning of each test run. These were given up as the reactor was each time detected well-sealed. Furthermore, without leakage tests the contact of catalysts with methane was avoided before achieving the desired reaction temperature.

In the most test runs the reactor was first heated to the desired temperature and after that the methane flow was turned on. In the experimental results this is characterized with decreasing methane conversion during the first 10 min. This decrease is related only to the response time of the experimental setup. In the other runs, characterized with increasing methane conversion during the first 10 min in the result charts, the methane flow was turned on already at temperatures of 300-500 °C and the reactor was heated stepwise to find the reactive temperature area of the catalyst. When the accuracy of the experiments is considered, the tests conducted with the first mentioned arrangement are better.

The produced carbon deposited both on the catalyst pellet surface, fell down on the reactor bottom, and deposited on the reactor walls. After each experimental run, the produced carbon was collected and weighed. The carbon deposition on the reactor walls was swept by using a metallic stick and a bottle brush.

4 RESULTS

The results achieved in the CDM experiments with four commercial catalysts are presented in this chapter. During the experiments the gas composition was analyzed with an FTIR at intervals of 30 seconds, and the methane conversions in Figures 4.1-4.3 were calculated from the experimental results as five-minute averages. The catalyst surface areas were proportional to catalyst 1 so that the relative apparent surface area of 1 is equal to the surface area of one nickel pellet (catalyst 1). The product carbon appearance was analyzed after each experimental run when it was collected from the experimental system. The used catalyst container (Ceramic/Kanthal) is marked in the legend of Figures 4.2 and 4.3 as described in chapter 3.3.

4.1 Catalysts' activity

Catalyst 1 was active at a temperature range between 500 and 700 °C. As high as 40 % methane conversion was observed at 700 °C. With the reactor in question, the thermal decomposition of methane was experimentally tested to begin at temperatures above 900 °C. However, catalyst 1 suffered a considerable drawback, as the catalyst pellets broke down during the experiments. A test run of 120 min at 700 °C in nitrogen atmosphere was conducted to confirm that the reason was neither the high temperature nor the rapid heat transfer. Most probably the explanation is related to the formation of whisker carbon that is presented more detailed in chapter 2.2.1.2.

The CDM reaction results with catalyst 1 are shown in Figure 4.1.

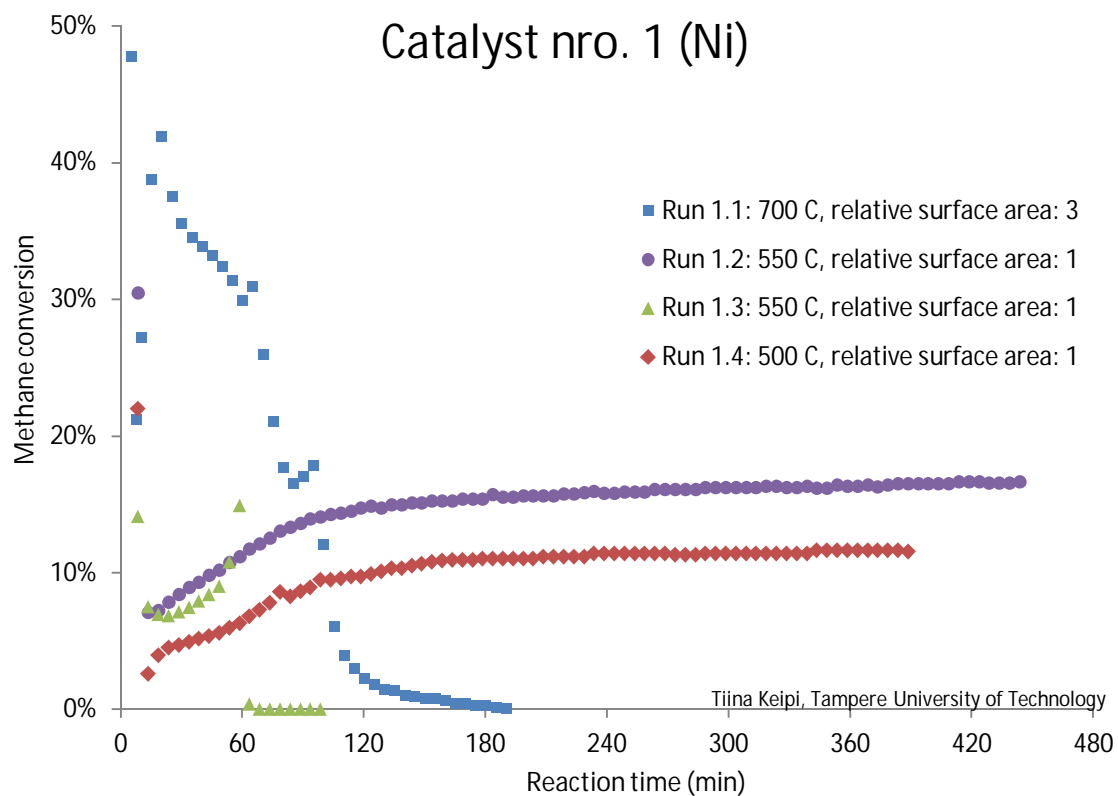


Figure 4.1. The results of the CDM tests with catalyst 1.

With the methane flow of 150 ml min^{-1} it took approximately 10 min before the reaction products reached the FTIR and the true conversion values were recorded. As shown in Figure 4.1, during the run 1.3 a sudden drop of methane conversion occurred after 60 min. This was related to the catalyst breakdown that was most likely caused by the formation of whisker carbon. After 60 min the catalyst pellet was half destroyed and it fell to the reactor bottom stopping the decomposition reactions. Run 1.1 show similar behavior as the catalyst pellets were broken and fallen one by one after reaction time of 20, 65, and 95 min.

Runs 1.2 and 1.4 have two clearly different parts. First 100 min the methane conversion was increasing indicating the reactivity increase, after which the methane conversion was stabilized. It is presumable that the produced carbon either catalyzes the decomposition reaction or promotes the catalytic activity of the Ni-catalyst.

When comparing to run 1.3, it is assumed that the catalyst pellets of runs 1.2 and 1.4 have totally destroyed after approximately 120 min, which is also the point of conversion stabilization. Contrary to the other curves, runs 1.2 and 1.4 remain the methane conversion after the assumed catalyst destruction. In these experiments no deactivation was detected and tests were stopped after 440 and 390 min. Continuation of these experimental runs would have probably resulted to the blocking of the reactor tube because of the carbon production.

The experimental results of the CDM tests conducted with catalyst 2 are shown in Figure 4.2.

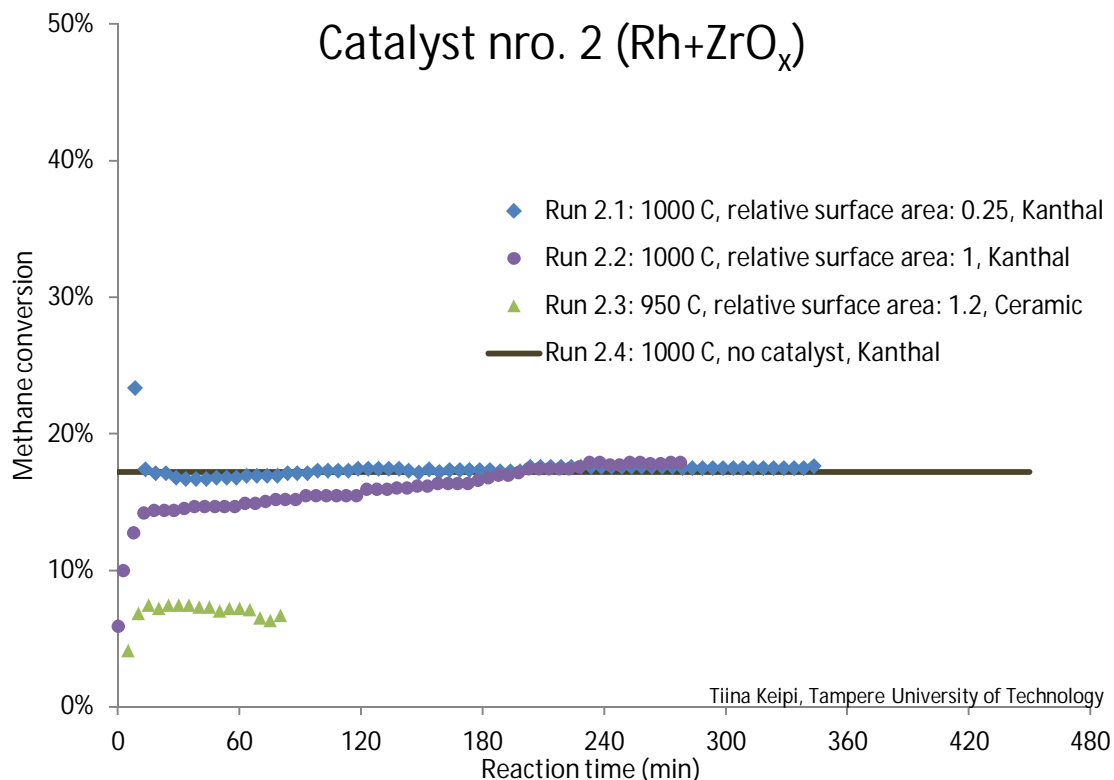


Figure 4.2. The results of the CDM tests with catalyst 2 and a test run without catalyst.

The reactivity of catalyst 2 was negligible at temperatures between 500 and 850 °C. At a temperature of 1000 °C the observed methane conversion was 15-17 %. However, this is equal with the results of a test run 2.4 at 1000 °C without any catalyst. Therefore, it is stated that catalyst 2 did not promote the methane decomposition reaction with this experimental setup.

The CDM tests were conducted with catalyst 3 at a temperature range of 300-1000 °C and the results are shown in Figure 4.3.

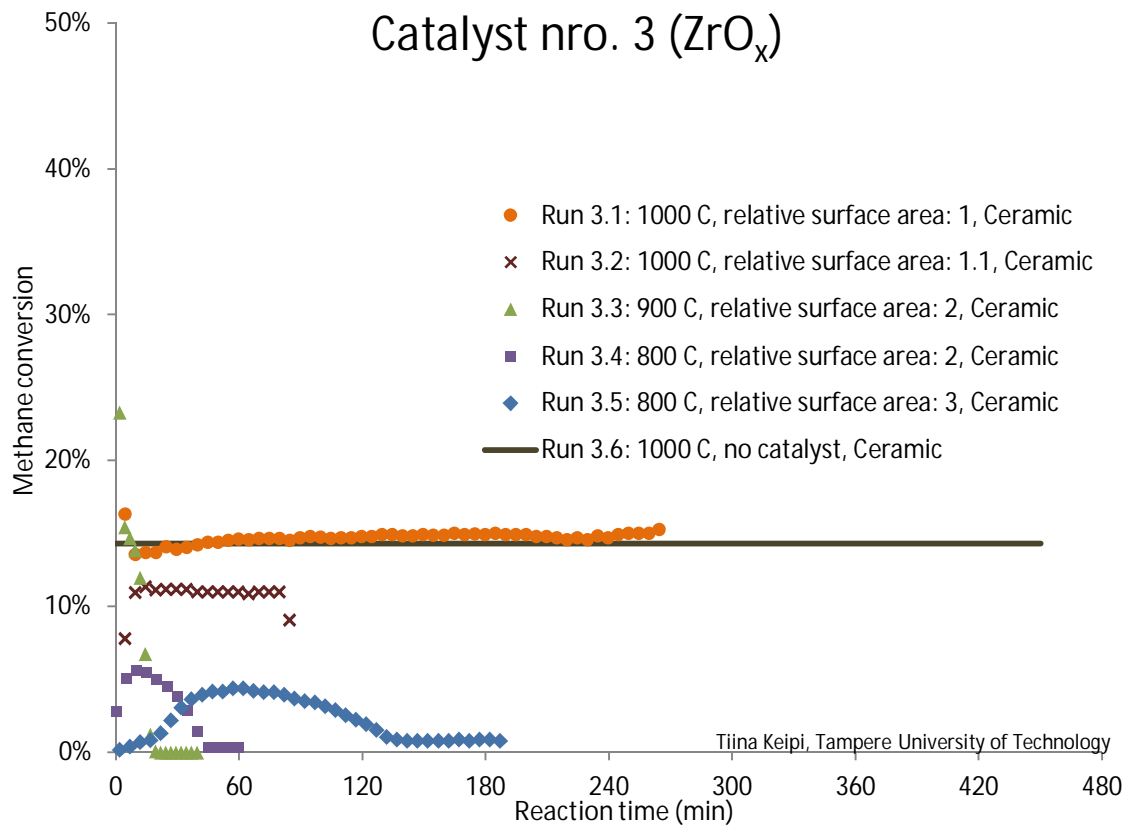


Figure 4.3. The results of the CDM tests with catalyst 3 and a test run without catalyst.

During the run 3.1 the methane conversion was around 15 % at 1000 °C, which is equivalent to the result of the test run without a catalyst (run 3.6). Therefore, catalyst 3 did not promote the reaction at 1000 °C. However, catalyst 3 reacted at a temperature of 800 °C (runs 3.4 and 3.5), but the catalyst deactivated rapidly as a result of carbon formation. At a temperature of 900 °C the instantaneous conversion was around 15 %, but a rapid deactivation occurred. In conclusion, with this experimental arrangement catalyst 3 showed a slight activity at temperatures 800–900 °C but the deactivation was rapid.

Catalyst 4 showed no catalytic activity with this experimental setup at temperatures between 500 and 850 °C. The form of catalyst 4, i.e., small grains with the diameter of 0.15-0.35 mm, was poorly suitable to the reactor type used. With a batch reactor the catalyst surface area was poorly utilized and the handling of small grains was challenging. Grained catalyst is better suitable for example to a fluidized-bed reactor.

4.2 Product gas

The concentrations of methane and other hydrocarbons in the reaction product gas were measured with the FTIR. The FTIR cannot detect the biatomic homonuclear molecules, such as N_2 and H_2 . Therefore, the methane conversion was calculated from the difference in the methane concentration during the experiments and at the stage where no reactions occur.

Besides methane, the product gas was observed to contain small amounts of other higher hydrocarbons (a few percent of the total methane flow at maximum).

4.3 Product carbon

The solid carbon product from CDM with catalyst 1 was clearly different than was produced with other studied catalysts. The solid carbon product of methane decomposition with catalyst 1 was black soot-like powder. It partly fell down to the reactor bottom and partly clustered around the catalyst pellet (shown in Figure 4.4).

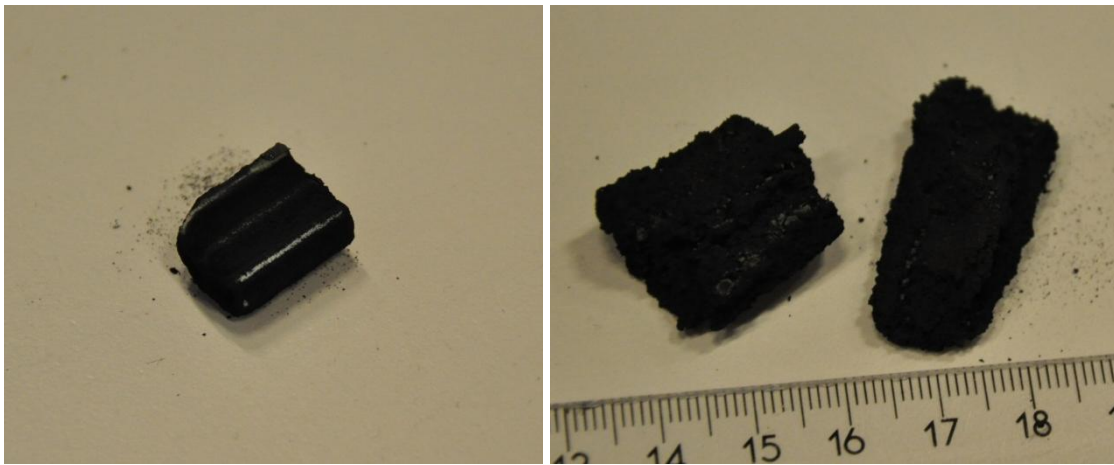


Figure 4.4. Partly destroyed catalyst 1 pellet after 60 min at 550 °C with methane flow of 150 ml min⁻¹ on the left, and a piece of the solid carbon product after CDM for 450 min at 550 °C on the right.

At the temperatures below 1000 °C, the solid carbon product of CDM with catalysts 2 and 3 formed a thin and dark grey layer on the catalysts' surface (shown in Figure 4.5). The carbon deposition isolated the catalyst pellets from the methane flow stopping the methane decomposition reactions.

At 1000 °C with catalysts 2 and 3 a carbon layer was formed also on the reactor inner surface (shown in Figure 4.5). However, in this reactor the thermal methane decomposition occurs at temperatures above 1000 °C. Therefore, at a temperature of 1000 °C the test runs without catalysts produced similar carbon deposition on the reactor walls than the CDM experiments with catalysts 2 and 3.

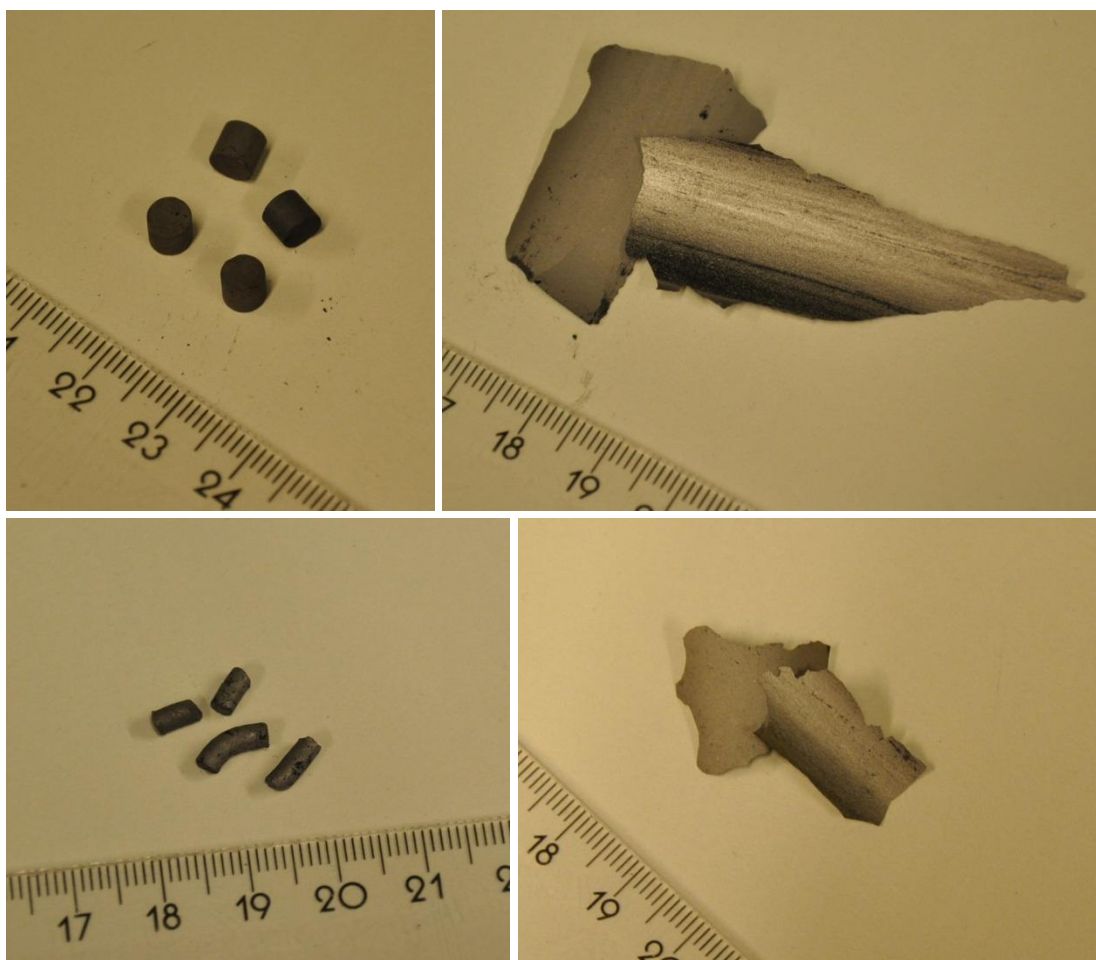


Figure 4.5. The upper row: Catalyst number 2 after 280 min at 1000 °C with methane flow of 150 ml min⁻¹ on the left, and a piece of the solid carbon product after the same experiment on the right. The lower row: Catalyst number 3 after 270 min at 1000 °C with methane flow of 150 ml min⁻¹ on the left, and a piece of the solid carbon product after the same experiment on the right. The public distribution of the catalyst pictures forbidden.

The product carbon of the CDM with catalyst 2 was rather tough and metallic. This is most likely related to the metallic Kanthal-basket used in these experiments as similar results were achieved also in a test run with the basket and without a catalyst.

4.4 Product carbon amount

The theoretical product carbon masses were compared to the experimented values in CDM experiments with catalyst 1 (Ni) in Table 4.1. Catalyst 1 is chosen to this investigation as it had a remarkable effect on the methane decomposition reaction and the carbon product was easily collected from the experimental system. The experimental carbon masses are simply weighed after each experimental run.

The theoretical product carbon masses were calculated as follows:

$$m(C) = \sum_{i=1}^k (\text{conversion}(i) * \Delta t) * \dot{n}(CH_4) * M(C) \quad (5)$$

where k is the number of points calculated from the experimental results at intervals of $\Delta t=5\text{min}$ (the sum expression is the piecewise calculated integral of the curves in Figure 4.1), \dot{n} is the methane molar flow rate in STP conditions, and $M(C)$ is the molar mass of carbon, i.e., 12.01 g mol^{-1} .

Table 4.1. *The theoretical and experimented product carbon masses in the CDM experiments with catalyst 1 (Ni). The experimental curves are shown in Figure 4.1.*

Run	Theoretical carbon (g)	Experimental carbon (g)
1.1: 700 °C, relative surface area: 3	2.2	0.6
1.2: 550 °C, relative surface area: 1	5.1	5.8
1.3: 550 °C, relative surface area: 1	0.3	0.3
1.4: 500 °C, relative surface area: 1	3.0	3.1

The experimental carbon masses corresponded fairly well to the theoretical values. As is shown previously in Figure 4.1, the run 1.1 was rather short and rapid changes in the methane conversion occurred during this experiment. Therefore, the theoretical carbon mass in this experiment was slightly too high compared to the experimental result.

5 DISCUSSION

In this study the influence of four commercial porous catalysts on methane decomposition was examined. Solid reaction products with a small particle size may easily block the pores of a porous catalyst and cause a rapid catalyst deactivation. According to the results, catalyst 3 (ZrO_x) catalyzed the reaction slightly at a temperature of 800 °C, but suffered from a rapid deactivation. Catalysts 2 ($\text{Rh}+\text{ZrO}_x$) and 4 (Ir) did not promote the reaction at temperatures between 500 and 1000 °C. Catalyst 1 (Ni) showed promising results as the methane started decomposing already at 500 °C. However, the nickel concentration in catalyst 1 was much higher than the concentrations of the catalyst metals in the other samples. This may partly explain the better catalyst properties of catalyst 1 compared to the other catalysts.

Furthermore, the results do not represent comprehensive and common facts about the reactivity of these catalysts. The results are linked with the experimental setup in question and the reaction conditions used in these experiments.

The results with nickel catalyst were promising both in terms of the relatively high methane conversion (10-40 %) at low temperatures (500-700 °C) and the long reaction times achieved (up to 7 h) without catalyst deactivation. It is possible that the increase of methane conversion during the first 100 min and the long reaction time in the two experimental runs were caused by the catalytic activity of the produced carbon. The nickel catalyst destruction during the experiments refers to the formation of whisker carbon (described more detailed in chapter 2.2.1.2). The nickel catalyst was reported as mechanically extremely tough. The forces related



to the whisker carbon formation on the catalyst surface and in the pores could explain the breakdown of the pellet.

The experiments left open the question how long the produced carbon can catalyze the methane decomposition reaction. Producing carbon with CDM is economically feasible when the used catalyst is cheap (as it could be destroyed in the process) compared to the value of the products. Therefore, it is necessary to study the amount of favorable products, i.e., hydrogen and carbon, that can be produced with a certain amount of the original catalyst.

6 RECOMMENDATIONS

According to the achieved results the methane decomposition reaction continued after the original nickel catalyst destruction. Therefore, further research is needed to find out how much carbon can be produced and how long the reaction can continue before the metal particles become totally isolated from the reaction. The autocatalysis in CDM is an interesting research area as a whole.

Besides the current experimental setup, the CDM with metal catalysts could be studied in a fluidized bed reactor. In fluidized bed the diameter of the catalyst particles should be equivalent to the grain size of the bed material (below 1 mm). Alternatively the catalyst material could be impregnated to the fluidization sand. An interesting issue would be to study how much the bed particles grind the deposited carbon away from the catalyst surface and how fast the catalysts would wear out.

To study the product carbon properties and different utilization possibilities, larger amounts of carbon should be produced. In practice this means a scale-up to a larger experimental setup. Also cooperation with different partners able to utilize the product carbon is needed to find out the required carbon properties. Ideas about possible new larger-scale experimental setup have been discussed.

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