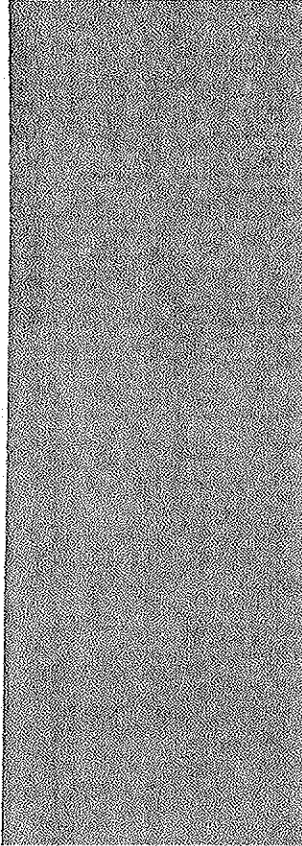
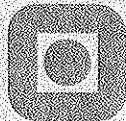


Marcus Fathi  
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of methane to synthesis gas



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The Norwegian University of Science and Technology  
Department of Chemical Engineering

**Catalytic partial oxidation of methane  
to synthesis gas**

by

**Marcus Fathi**

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This work is a direct continuation of the Dr. ing. thesis of Karina Heitnes Hofstad. It should not be necessary to point out the importance her work has had for the progress of mine. I therefore just wish to state my respect for what was already at the table when I started.



Marcus

*“Experience is a wonderful thing. It enables you to recognize a mistake when you do it again.”*

## Abstract

Hydrogen and carbon monoxide can be formed from the catalytic direct partial oxidation of methane without going through reforming processes. This has been shown experimentally with a Pt/Rh gauze catalyst at short contact time conditions with incomplete reactant conversions at high temperatures. However, the experimental data also shows that the yield of syngas through such a direct route is limited because the products are more reactive for combustion than the reactant methane.

The reactivity of adsorbed oxygen species towards oxidation of the various synthesis gas components was further studied in detail. It was found necessary to attempt to constrain the supply of oxygen to the active sites in order to suppress the combustion processes. It was found that at conditions used for the partial oxidation of methane, platinum does not only adsorb oxygen on the surface, but oxygen is also absorbed into the bulk of the metal. This implies that the active sites on the surface can be supplied with oxygen not only by gas phase adsorption, but also by solid diffusion from the metal bulk. The latter being very slow compared with the former. It was found that the selectivity to carbon monoxide and hydrogen increased drastically in absence of gas phase oxygen, when oxygen was supplied to the active sites uniquely by solid diffusion.

The partial oxidation of methane in the absence of gas phase oxygen was further studied using Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> as an intermediate solid oxygen reservoir. This material was treated in cycles of methane and oxygen. The γ-Al<sub>2</sub>O<sub>3</sub> provided high surface area and thereby good contact between the reactant gases and the solid material. The cerium oxide provided a suitable dynamic oxygen reservoir and the presence of platinum gave high activity for the conversion of methane. The results showed that synthesis gas could be formed with high selectivity and at full conversion of methane from the gas-solid reaction at temperatures as low as 700 °C. The solid material was easily regenerated with oxygen.

## List of publications

### Articles

This thesis is based on the following articles referred to in the text by their Roman numerals. Reprints of the articles and manuscripts are given as appendices I-V.

- I M. Fathi, K.H. Hofstad, T. Sperle, O.A. Rokstad and A. Holmen, "Partial oxidation of methane to synthesis gas at very short contact times", *Catalysis Today* 42 (1998) 205
- II M. Fathi, O.A. Rokstad and A. Holmen, "Partial oxidation and steam reforming of methane over platinum/rhodium metal gauze catalysts at very short contact times", *Manuscript accepted for publication in Catalysis Letters*.
- III M. Fathi, F. Monnet, Y. Schuurman, A. Holmen and C. Mirodatos, "Reactive oxygen species on platinum gauze surfaces during partial oxidation of methane", *Journal of Catalysis* 190 (2000) 439
- IV M. Fathi, E. Bjørgum, T. Viig and O.A. Rokstad, "Partial oxidation of methane: Elimination of gas phase oxygen", *in press, Catalysis Today*
- V J.C. Jalibert, M. Fathi, O.A. Rokstad and A. Holmen, "Synthesis gas production from methane with promoted cerium oxide by a cyclic gas-solid reaction", *Manuscript in preparation*.

During this work, the author has also contributed to other publications dealing with related topics that do not fit directly under the title of this thesis. These are therefore not part of the fundament for this thesis:

- M. Fathi, R. Lødeng, E. Nilssen, B. Silberova and A. Holmen, "Short contact time oxidative dehydrogenation of propane", *in press, Catalysis Today*
- M. Fathi, E. Bjørgum and O.A. Rokstad, "Anaerobic conversion of ethane with promoted cerium oxide", *Manuscript in preparation*
- R. Lødeng, M. Barré-Chassonnery, M. Fathi, O.A. Rokstad and A. Holmen, "Carbon formation from Decomposition of CH<sub>4</sub> on supported Ni Catalysts", *Stud. Surf. Sci. Catal.* 111 (1997) 561

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**Oral Presentations at international meetings**

The following oral presentations have been given at international meetings based on results produced during this work:

M. Fathi, K.H. Hofstad, T. Sperle, O.A. Rokstad and A. Holmen, "Partial oxidation of methane to synthesis gas at very short contact times", Oral presentation, Third Workshop on C1-C3 Hydrocarbon Conversion, Krashoyarsk, Russia 1997

M. Fathi, K.H. Hofstad, O.A. Rokstad and A. Holmen, "Catalytic Partial oxidation of methane to synthesis gas on gauze catalysts", Oral presentation, 5<sup>th</sup> European Workshop on Methane Activation, Limerick, Ireland 1997

M. Fathi, O.A. Rokstad and A. Holmen, "Partial oxidation and steam reforming of methane over Pt/Rh metal gauze catalysts", Oral presentation, 8<sup>th</sup> Nordic Symposium on Catalysis, Oslo 1998

M. Fathi, E. Bjørgum, T. Viig and O.A. Rokstad, "Partial oxidation of methane: Elimination of gas phase oxygen", Oral presentation, Asian-Pacific Congress on Catalysis (APCAT 2000), Sydney 2000.

B. Silberova, M. Fathi, E.S. Nilsen, R. Lødeng and A. Holmen, "Oxidative dehydrogenation of propane at short contact time", Oral presentation, 14th International Congress of Chemical and Process Engineering (CHISA), August 2000, Prague, Czech Republic



**The author's contribution**

In papers I, II and III the author has planned, conducted and interpreted all experiments as well as writing the entity of the articles. In paper III, Yves Schuurman was very much involved in both the experimental work and the writing of the paper.

For paper IV the author participated actively as supervisor in the experimental planning and interpretation of the results and wrote the article text. For paper V the author participated actively in the experimental planning and in the interpretation of the results. The author also contributed significantly to the writing of the article text.

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## 1 Introduction: Chemical conversion of natural gas

### 1.1 Natural gas: resources, production and application

The following paragraph is based on information from The Norwegian Ministry of Petroleum and Energy [1] together with worldwide statistical data from British Petroleum - Amoco [2]

The Norwegian proven gas resources by the end of 1999 were 3,100 billions  $\text{Sm}^3$ . This represents about 2 % of the proven world resources (146,000 billions  $\text{Sm}^3$ ). The natural gas production from the Norwegian continental shelf is approximately 43 billions  $\text{Sm}^3/\text{year}$  (1998) whereof less than 0.7 billion  $\text{Sm}^3/\text{year}$  (<2%, 1998) is used locally for methanol production at Tjeldbergodden. The rest is piped from Kårstø and Kollsnes to Emden (Germany), Zeebrugge (Belgium) and Dunkerque (France). The sales of natural gas to Western Europe is expected to level out at about 78-80 billions  $\text{Sm}^3/\text{year}$  in the coming decade which will represent 17% of the Western European consumption (480 billions  $\text{Sm}^3/\text{year}$  in 1998). In 1998 the worldwide production of natural gas was 2,380 billions  $\text{Sm}^3$ . The Norwegian production will therefore represent 3-4% of the world production. The Norwegian reserves are located very far from the market in Western Europe. Some of the resources are also present as associated gas in remote oil fields and complicates the production of oil from these fields. Flaring of light components in petroleum is strictly demotivated on the Norwegian continental shelf by emission taxes, especially after the Kyoto Agreement in December 1997. The possibility of converting natural gas to liquids and easily transportable feedstocks/fuels has been a field of interest in Norwegian research since the initiation of the SPUNG program in the late 1980ies (State Program for Utilization of Natural Gas) and the Natural Gas Conversion program in the late 90ies.

The natural gas on the Norwegian continental shelf consists mostly of methane (80-85%). The most important large-volume liquid products from methane are methanol and ammonia. Synthetic fuels can also be produced from methane by Fisher Tropsch (F-T) synthesis but the low petroleum prices during the last decades have not motivated large production of synthetic fuels. Presently, this technology needs long term petroleum prices above 25 US\$/barrel to be competitive. There could, however,

be other economic incentives behind F-T production such as negatively priced associated natural gas and transport cost benefits of liquids versus piping of natural gas.

The world production of methanol was in 1998 approximately 20 Mton/year whereof 0.8 Mton/year (4%) were produced at Tjelbergodden, Norway. A few years ago the demand for methanol was expected to increase largely because its derivative, MTBE, was suitable to replace lead and aromatic compounds in gasoline. However, MTBE turned out to be non-biodegradable and was therefore considered environmentally disadvantageous due to risk of groundwater contamination. Future possible large-scale methanol consuming processes are the MTO process in which methanol is converted to light olefins and the MTG process where methanol is converted to gasoline fuel. Methanol is itself a fairly good fuel or fuel additive with an octane number (RON) of 112.

The world production of ammonia was in 1998 approximately 200 Mton/year. The largest application of ammonia is as feedstock to make nitrates and urea in synthetic fertilizers. The production volumes on world basis of ammonia and methanol are large but represent a consumption of no more than 2% of the annual worldwide natural gas production. Natural gas is therefore primarily an energy source.

Hydrogen is considered to be the "clean fuel of the future". Methane is the most hydrogen rich hydrocarbon and is therefore a good potential hydrogen source. In the recent years, there has been increased attention towards hydrogen production.

- New European directives on fuel quality have caused petroleum refineries to change from having excess hydrogen to become net hydrogen consumers.
- Hydrogen as a feedstock for fuel cell running electric cars has led to attention towards small-scale *in situ* syngas/hydrogen production from all kinds of transportable fuels.
- Syngas (hydrogen) based power plants have been proposed in order to reduce emissions of carbon dioxide. These power plants have been suggested to run on hydrogen fueled turbines based on syngas similar to what is applied for ammonia production ( $H_2/N_2 = 50/50 - 75/25$ ). Carbon dioxide absorption upstream of the turbines makes long term storage (sequestration) possible by reinjection into

suitable geological formations. Such power plants will be more capital intensive than conventional plants and the energy efficiency will be significantly reduced due to large energy consumption in carbon dioxide separation and recompression. Profitability of such power plants will therefore largely depend on the politically given economic framework.

## 1.2 Syngas

Production methanol, ammonia or F-T fuels always goes through the same first step. The hydrocarbon feed (methane) is converted to synthesis gas (syngas), which is a reactive mixture of carbon monoxide and hydrogen (and in certain cases nitrogen). The exact composition depends on what final product the syngas is intended for. The conversion of hydrocarbons into syngas is a mature technology, well-developed in industrial applications. There are several different commercially available technologies. The choice of technology depends strongly on scale and on the desired syngas composition.

### 1.2.1 Tubular steam reforming of methane

Steam reforming is the most common way to produce synthesis gas [3-6]. Steam and hydrocarbons are endothermally converted to carbon monoxide and hydrogen. This process requires large heat input and high temperatures are necessary in order to obtain good conversion and selectivity. Steam reforming is done in tubular reactors where external burners fueled by parts of the hydrocarbon feedstock supply the necessary heat of reaction. All commercial plants are based on supported nickel catalyst systems often promoted with oxides of metals such as magnesium or potassium. The rate of heat transfer into the reforming tubes where the reactions take place is very important. The rate of heat transport into the tubes is even considered to be rate determining for the reactor performance.

The feedstock for tubular steam reformers is usually methane and excess steam to prevent carbon formation. The  $\text{CH}_4/\text{H}_2\text{O}$  feed ratio ranges from 1.5 to 4.0. The inlet temperature is usually 450-650 °C and the exit temperature is 750-900 °C. The operating pressure ranges from 15 to 40 bar. Most downstream processes operate at

relatively high pressures. A high operating pressure in the steam reformer is therefore desired in order to reduce syngas compression costs. However, high operating pressure is thermodynamically disadvantageous for the methane conversion and makes it necessary to compensate with higher reaction temperatures. Typical space velocity for a steam reformer unit is around  $1400 \text{ volCH}_4/\text{h} \cdot \text{vol}_{\text{reactor}}$  [7]. The product gas from a conventional steam reformer has a  $\text{H}_2/\text{CO}$  ratio between 2.5-3, which is too high for methanol and F-T synthesis. The  $\text{H}_2/\text{CO}$  ratio can be reduced by adding carbon dioxide to the feed gas [4].

Syngas production by steam reforming is considered to be a very capital intensive process. The process has good energy and carbon efficiency [3], but this has its cost in terms of large heat-transfer area and expensive steel alloys that can withstand the high temperatures and pressures involved. Syngas production by steam reforming usually takes as much as 50-70% of the total investment cost of a methanol plant [8,9].

Steam reforming in tubular reactors requires heat input at above  $900 \text{ }^\circ\text{C}$ . This is provided by combustion of natural gas outside the reforming tubes. The exhaust gas from these burners is very hot and a large energy source for steam generation, gas preheating and other downstream applications. Additional steam is recovered from the hot product stream in a waste heat boiler. Tubular steam reforming therefore gives very advantageous utilities. The choice of technology for syngas production can therefore also be motivated by utility and energy needs in downstream processes. Cogeneration of electrical power is also possible in combination with tubular steam reforming [10].

### **1.2.2 Partial oxidation of methane**

Partial oxidation of methane usually refers to the production of carbon monoxide and hydrogen from methane and oxygen or air. The desired reaction is slightly exothermic, but suffers from severe selectivity problems due to the strongly exothermic combustion reactions that can occur between methane and oxygen both homogeneously and heterogeneously. The combustion "problem" has been solved in industrial application simply by letting it proceed and use the generated heat for endothermic steam and dry reforming of unconverted reactant. The endothermic

reforming reactions can take place homogeneously at high temperatures but can also be catalyzed towards equilibrium by a heterogeneous catalyst. Two different reactor types (POX and ATR) will be further described below.

### 1.2.3 Partial oxidation by non-catalytic autothermal reforming (POX)

In a POX reactor, preheated methane and oxygen are fed into an empty insulated reactor vessel where combustion is ignited and the heat that is released causes methane reforming to take place. The non-catalytic partial oxidation of methane needs high temperatures to ensure high methane conversion and to reduce soot formation [11]. In such a reactor, both total and partial combustion occur together with endothermic reforming reactions at temperatures around 1100-1500°C. The  $O_2/CH_4$  feed ratio is about 0.7-0.75 which is higher than the stoichiometric ratio for the ideal partial oxidation of methane. The reactor operates autothermally without direct heat input/output to/from the reaction zone. The advantages of this reactor are its simplicity and the ability to operate at high pressures. The cost of an oxygen plant is considerable.

### 1.2.4 Partial oxidation by catalytic autothermal reforming (ATR)

Autothermal catalytic reforming is in principle very similar to a POX reactor. The combustion reactions occur homogeneously in a carefully designed burner. Immediately downstream of the combustion zone, there is a nickel-based catalyst that catalyzes both steam and dry reforming of unconverted methane. Such a reactor gives better performance than a POX reactor because it does not need the high temperatures necessary for the reforming reactions to occur homogeneously. The nickel catalyst provides good approach to equilibrium of the product gases. The exit temperature is usually around 1050 °C. Steam is usually added to the feed together with methane and oxygen to prevent formation of carbon in the catalytic zone of the reactor. The steam/carbon ratio must be higher than 0.6 [12]. The oxygen feed can be pure oxygen, enriched air or air. However, syngas dilution in nitrogen from air is unwanted in the synthesis of methanol since methanol reactors operate at pressures significantly higher than in the syngas production equipment. The methanol synthesis is a recycle process, which also makes inert dilution unwanted. The cost of an oxygen plant is considerable and makes ATR technology largely subject to economy of scale.



### **1.2.5 Combined steam reforming and autothermal reforming**

The choice of technology for synthesis gas production is strongly dependent on the downstream application. Conventional steam reforming gives a very hydrogen-rich synthesis gas. The conditions under which the steam reformer operates are also dictated by the methane slip tolerable for the downstream process. Inerts such as methane are not wanted in most of these processes because they lead to unnecessary compression and recycle costs. Methanol and F-T synthesis also require a syngas with a  $H_2/CO$  ratio close to 2.0 which is considerably lower than what is given by a steam reformer. In the case of methanol synthesis, there is a very good synergy effect by combining a steam reformer and an autothermal reformer in series [13]. The  $H_2/CO$  ratio in the syngas can be regulated to the desired value by the oxygen/steam feed to the ATR and by carbon dioxide recycle to the steam reformer feed. When methane slip no longer is crucial from the steam reformer, it can be operated under very mild conditions and its size is significantly reduced compared with a stand-alone reformer. The operating pressure can also be increased leading to significantly reduced syngas compression costs.

### **1.3 Scope of this work**

This work was initiated to study the partial oxidation of methane at different conditions. The direct reaction between methane and oxygen on catalytic surfaces was of particular interest.

A great deal of work was conducted by Karina Heitnes Hofstad prior to the initiation of this study. [14-19]. The reactivity of surface oxygen and its role in the reaction pathway was already at this point identified as the most interesting topic for further studies.

## 2 Theory and relevant literature

Karina Heitnes Hofstad, [19] made a review and summary of the literature concerning the catalytic partial oxidation of methane in 1996. This chapter will therefore only give a brief introduction to the relevant  $C_1$  chemistry and cover the literature that has direct relevance for this particular study.

### 2.1 Methane and oxygen: Reactions and thermodynamics

As will be explained in further detail later, two mechanisms for the catalytic partial oxidation of methane have been proposed in the literature. A: Direct partial oxidation of methane to synthesis gas and B: Total oxidation of methane followed by steam and carbon dioxide reforming. The question of whether or not carbon monoxide and hydrogen are primary products of the methane oxidation has been debated in the literature. This chapter will cover the energetics and kinetics of the different processes involved in the high-temperature  $C_1$  chemistry involving oxygen.

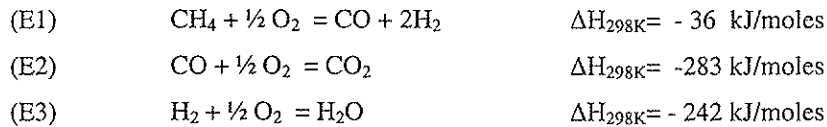
The stoichiometry of the partial oxidation of methane implies a feed ratio of methane and oxygen of 2:1. This gives an atomic C:O:H ratio of 1:1:4. The high temperature  $C_1$  chemistry involving oxygen and hydrogen can briefly be divided into two categories; oxidation processes and reforming processes. The enthalpies involved in the different reactions are given in E1-E9. Total oxidation of methane is strongly exothermal whereas reforming of methane is strongly endothermic.

The product or reactant molecules in the  $C_1$  chemistry are either highly stable or highly reactive. Carbon dioxide and water are both very stable molecules and energetically very favorable, whereas carbon monoxide and hydrogen both have large potential energies that can be released by reaction with oxygen. This makes the reaction enthalpies involved in the  $C_1$  chemistry quantitatively very large.

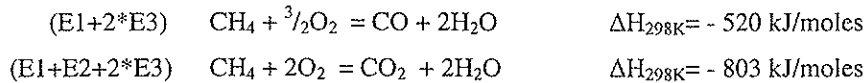
All the involved oxidation reactions (E1, E2 and E3) are exothermal. The partial oxidation of methane (E1) is just slightly exothermal whereas the secondary oxidation reactions (E2 and E3) are strongly exothermal. The exothermicity of the total

combustion (E1+E2+2\*E3) is therefore first of all connected to the formation of carbon dioxide and water. The first oxidation of methane to carbon monoxide and hydrogen involves hydrogen formation from the strongly endothermal methane decomposition (E6) and is therefore not as exothermal as the further oxidation of carbon monoxide and hydrogen to carbon dioxide and water (E2 and E3). Furthermore, the energy release in the first oxidation of carbon to carbon monoxide (E9) represents less than half the energy release as compared to the second oxidation to carbon dioxide (E2).

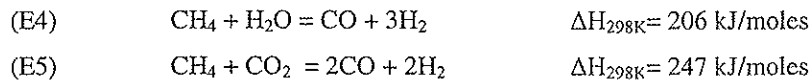
**Oxidation:**



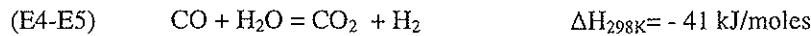
**Partial and total combustion:**



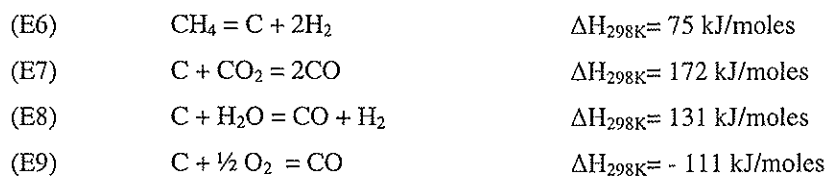
**Reforming:**



**Water-gas shift:**



**Carbon formation and gasification:**



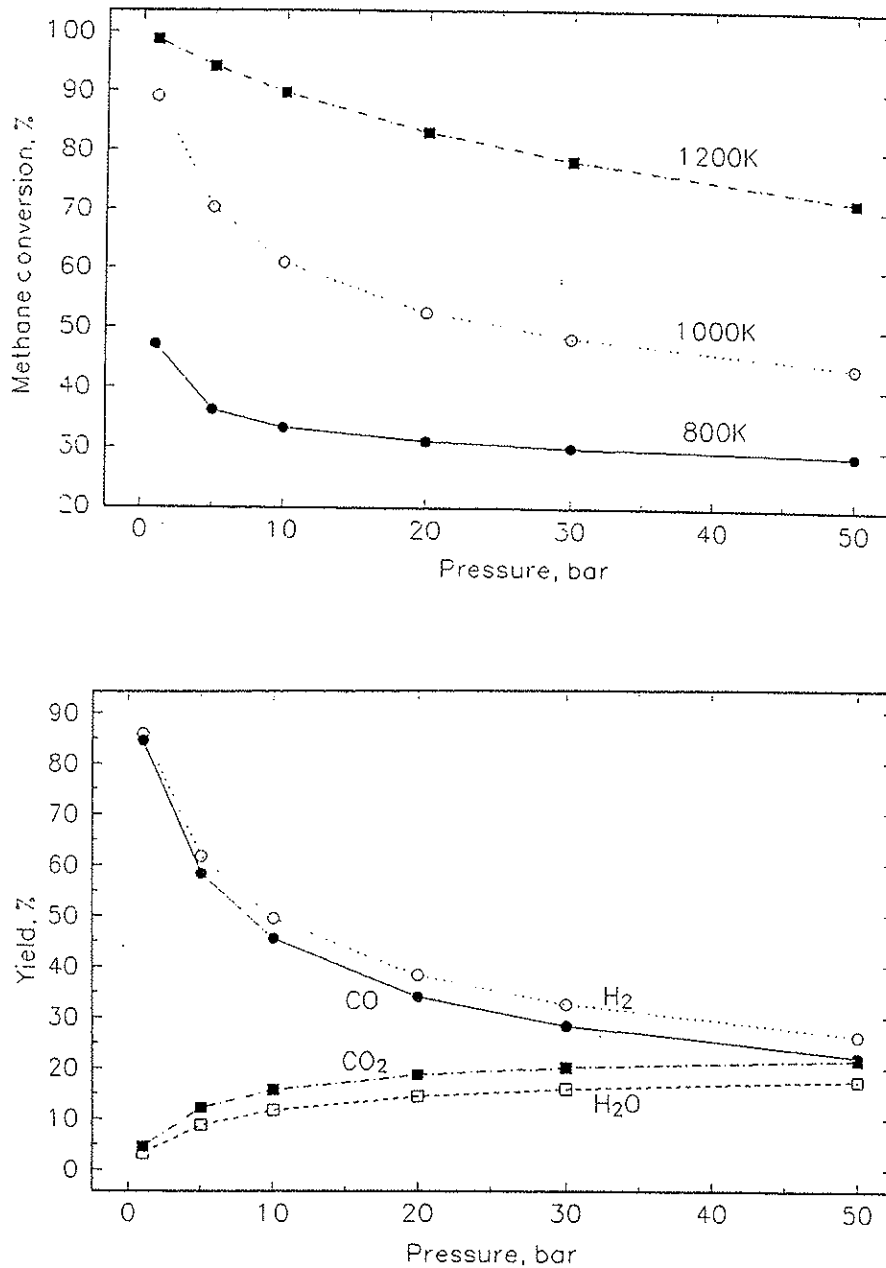
In the total combustion of methane, the oxidation of carbon to carbon dioxide represents 394 kJ/moles whereas the oxidation of hydrogen to water represents 484 kJ/moles. Most of the energy from methane combustion can therefore be said to be a

result of the formation of water rather than carbon dioxide. For hydrocarbons that are less rich in hydrogen than methane, the energy is more a result from the oxidation of carbon.

Both steam (E4) and carbon dioxide (E5) reforming are strongly endothermal processes. These reactions involve dissociation of water and carbon dioxide, which is energetically very unfavorable. The endothermicity of these reactions can mainly be ascribed to the energy requirement of bringing the total oxidation products, carbon dioxide and water, back to the partial oxidation products carbon monoxide and hydrogen.

When exposing a mixture of methane and oxygen to high temperatures, ignition of combustion processes is inevitable. The material balance given by the methane to oxygen feed ratio determines the extent of combustion. When feeding methane and oxygen in the ratio of 2:1, the methane conversion is limited by the material balance to 25% in the case with total combustion and to 33% in the case with partial combustion. This means that if combustion occurs with a feed for partial oxidation of methane, the oxygen conversion will reach 100% when 67% or more of the methane feed remains unconverted. The adiabatic temperature increase caused by this combustion can easily be calculated and depends on the degree of dilution and the ratio of total combustion versus partial combustion.

Several studies of the thermodynamics in the partial oxidation of methane have been published [19-25]. Therefore only very simple relations will be pointed out here. The thermodynamic effect of temperature on the  $C_1$  chemistry can qualitatively be seen from the reaction enthalpies. High temperature of reaction will tend to favor partial combustion on behalf of total combustion. High temperatures during methane combustion are inevitable due to the large energy release by both partial and total combustion. If combustion takes place, most of the methane must be converted subsequently by steam or carbon dioxide reforming which are both strongly endothermic processes. High temperature of reaction favors both the methane reforming processes and is necessary in order to obtain high methane conversion and high synthesis gas selectivity.



*Figure 2.1: Equilibrium methane conversion at different temperatures and pressures (upper figure) and product yields at different pressures at 1000 K (lower figure) in a mixture of  $\text{CH}_4:\text{O}_2:\text{N}_2=2:1:4$ . Rokstad et al. [25].*

Water-gas shift (WGS, E4-E5) must also be taken into account when considering this system. The reduction of water by carbon monoxide is a slightly exothermal process. Reverse water-gas shift is the reduction of carbon dioxide by hydrogen which would require energy input. At high temperatures the WGS is shifted to the left which gives water and carbon monoxide. At low temperatures WGS equilibrium predicts formation of carbon dioxide and hydrogen.

Figure 2.1 shows some equilibrium data for methane conversions and product yields.

Pressure is an important parameter in syngas production. Most downstream syngas processes are performed at high pressure and it is therefore also desirable to perform the syngas production at as high pressure as possible to reduce syngas recompression costs. The thermodynamic effect of pressure is less obvious than the effect of temperature, but some simple thumbnail rules can be deduced from the reaction stoichiometry. Partial oxidation of methane to carbon monoxide and hydrogen (E1) is a mole-increasing process and will be disfavored by high pressure. Combustion is favored by high pressure. Water-gas shift is not affected by pressure. Both the reforming processes (E4 and E5) are disfavored by high pressure. Therefore, the main thermodynamic effect of pressure on this system is that high pressures favor deeper oxidized products and lower methane conversion. If one set of values for equilibrium conversion and selectivity is obtained at a given pressure and temperature, an increase in the pressure must be accompanied by an increase in the temperature in order to compensate for the negative effect of the higher pressure (Fig. 2.1).

In addition to the energetic differences between combustion and reforming processes based on functions of state, there are also kinetic differences between these two processes. Oxidation processes are known to proceed much more rapidly than reforming reactions. The thermal effects of whether a process is exothermic or endothermic also affect the kinetics indirectly. Endothermic processes require heat input to maintain the reaction rate. Heat input rate can thereby become rate determining for the reactor performance in strongly endothermic processes. Exothermic processes such as combustion of methane can proceed autothermally and are not dependent on external heat input. The activation energies of dissociating water and carbon dioxide are very high both homogeneously and heterogeneously. Slow

oxidant dissociation makes reforming processes slower than oxidation processes. It has been proposed that at extremely low residence time, the initial partial oxidation of methane (E1) can be performed selectively without the influence of neither secondary combustion reactions (E2 and E3) nor reforming processes (E4 and E5). Therefore many researchers have studied the oxidation of methane in short contact time catalytic reactors. These reactors are often operated at high temperatures and with low pressure-drop catalyst systems that enable extremely high reactant throughputs.

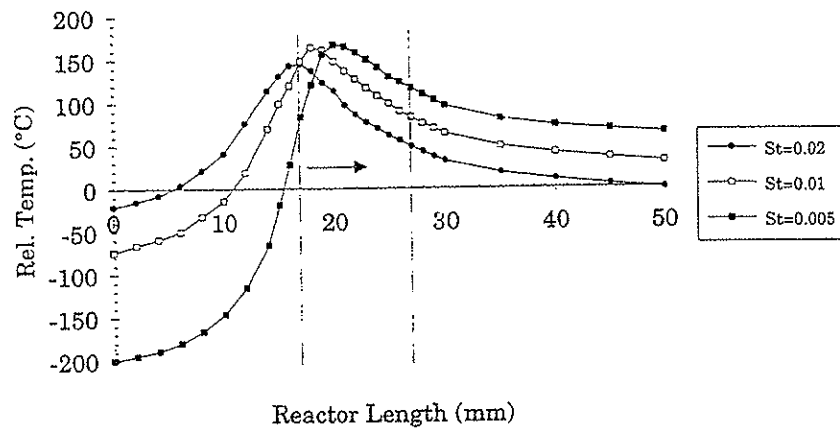
## **2.2 Short contact time catalytic partial oxidation of methane**

This area of research was pioneered by Schmidt and coworkers at the University of Minnesota, USA. Most of the work deals with the partial oxidation of methane to syngas at very short contact times, but some studies also included other light alkanes such as ethane and propane [26-29].

The partial oxidation of methane was studied at very short contact times over noble metal gauzes and noble metal coated monoliths (both extruded cordierite and alumina foams). Strongly exothermic reactions gave very high temperatures of reaction. The reactor was operated at near atmospheric pressure with and without feed preheating. The contact times with the monolithic catalysts were as low as below 1 ms with the noble metal gauzes and in the range of 5-20 ms with the ceramic monoliths. The noble metal weight loading on all the monolithic catalysts studied by Schmidt and coworkers was always very high (12-20 wt.%). Synthesis gas was produced with high selectivity at full conversion of oxygen and high conversion of methane (>80%). Mass transfer limitations were identified to play a major role for both conversion and selectivity at these conditions [30,31]. Direct formation of synthesis gas from methane and oxygen was suggested [31-34] and a kinetic model based on the direct partial oxidation mechanism was developed [35-37]. Rhodium was found to be superior to platinum concerning the selectivity to synthesis gas. It was proposed that this was related to that the rate of hydroxyl formation is significantly slower on rhodium than on platinum surfaces and thus resulting in a lower activity for hydrogen combustion. It was also found that monolithic structures made from foams performed better than extruded materials. This was assigned to that mass/heat transfer and back mixing caused by convection is better in foam monolith structures than in straight channel

monoliths. The research performed by Schmidt and coworkers resulted in many patents, ex. US patent 5-648-582 [38].

There are, however, a few remarks that must be mentioned in context of noble metal monolithic catalysts for the partial oxidation of methane: Firstly, all the experimental results reported from Schmidts group are obtained using very high metal weight loadings. Some surface roughening was reported on the noble metal gauze catalysts, but the activity and ageing of the coated monoliths were not very much in focus. Noble metal volatilization is a well-known phenomenon in oxidation processes at very high temperatures [39-45] and could be crucial for the economy of a process based on very expensive metals such as platinum and rhodium. Secondly, there have been disagreements about the mechanism of syngas formation over such systems. The mechanism will be further discussed below, but there is only one important issue that has to be emphasized at this point.



*Figure 2.2: Temperature profiles through a monolith catalyst at various space times during partial oxidation of methane. The monolith catalyst was made from cordierite washcoated with  $Pt/Al_2O_3$ . The temperatures are relative to the external furnace temperature which was  $600^\circ C$ . K. Heitnes Hofstad and coworkers [14].*



The temperature profile along a monolithic catalyst structure is very important for the mechanistic interpretation of the results. Especially when dealing with this particular system that includes both strongly exothermic and strongly endothermic processes. The temperature measurements in the results presented by Schmidt and coworkers are limited to the exit temperature at the outlet of the active catalyst monolith. The temperature profile inside a monolithic catalyst during partial oxidation of methane is strongly depending on a number of parameters. Most important is the catalyst relative activity for the various reactions involved, together with the flow rate and heat input/output. Other researchers [14,15] have reported internal temperature maxima inside a monolith structure that are as much as 150 °C above the exit temperature (Fig. 2.2). It has been shown that strongly exothermic combustion processes can occur inside the catalyst without to a large degree affecting the exit temperature of the monolith. Strongly endothermic processes such as steam and carbon dioxide reforming cause the temperature to rapidly decrease downstream of the combustion zone.

As mentioned, similar studies with both transition metal (Ni, Pd, Pt) coated ceramic monoliths [14,15] and noble metal gauze catalysts [15-17,46] have been reported. Heitnes Hofstad [14-17,19] used a reactor that allowed temperature profiles throughout the whole reactor to be recorded. As mentioned above, the temperature profiles showed huge gradients inside the monolith structures. Noble metal (Pt) volatilization and migration/loss from the catalyst was also shown to take place [16,17]. Platinum deposition was found by EDS (energy dispersive X-ray spectrometry) downstream of a Pt gauze used for partial oxidation of methane for only a few hours on stream at high temperatures (>900 °C). Gauzes made from Pt/Rh alloys were shown to have better stability with time on stream and less tendency of metal loss.

De Smet and coworkers [46] studied the partial oxidation of methane at atmospheric pressure over platinum metal gauze catalysts at very short contact times (0.02-0.2 ms) and at relatively high temperatures (<950 °C). Very low selectivity to hydrogen was observed at these conditions. Both mass and heat transport limitations were found to play a major role. A flat-plate reactor model was developed and the series-parallel mechanism enabled computer simulation of the experimental results.

### 2.3 Transient kinetic studies of the reaction mechanism

Mechanistic and kinetic studies of the catalytic methane oxidation are challenging for many reasons. Firstly, the exothermicity of the combustion reactions causes very high temperatures of reaction. Secondly because the combustion reactions are very rapid. These two complications make it very hard to operate a catalytic reactor without temperature and concentration gradients. Attempts have been made with high feed and catalyst dilution, but hot spots are always likely to occur, even in these systems. There are, however, a few transient kinetic studies that provide some qualitative information about the oxidation of methane on platinum and rhodium surfaces [9,18,47-53]. These studies have been performed in TAP (Temporal Analysis of Products) reactors similar to the setup described later in Chapter 3. Multifunctional TAP reactors have been found suited for detailed studies of methane oxidation for many reasons. Firstly, the good time resolution enables studies of very rapid reactions such as methane oxidation. Secondly, the TAP-reactor is operated under vacuum with only Knudsen diffusion and thereby: By definition there is no contribution from gas phase reactions. Thirdly, the vacuum in the TAP reactor together with the fact that there are very few molecules that react enables the catalyst to be studied without temperature gradients. It was also believed that concentration gradients were avoided, but this is further discussed and shown not necessarily to be evident in paper III.

There are, however, some important experimental differences in these studies with the older TAP system and the present study in paper III that was performed in a new high temperature TAP-2 reactor. This concern the temperature of reaction and the distance between the catalyst bed and the quadrupole mass spectrometer and will be further discussed later. The interpretation of the results is also quite different in the present study.

Catalytic partial oxidation of methane over Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh black was studied by Buyevskaya and coworkers [47,48]. It was found that on both supported and unsupported rhodium, the reaction pathway was strongly affected by the degree of surface reduction. Lattice oxygen was also found to participate in the reaction pattern. It was concluded that even though hydrogen could be formed from the decomposition

of methane, the reaction mechanism during steady-state operation was indirect; meaning that synthesis gas was formed from reforming of methane by carbon dioxide and water. Partly oxidized univalent rhodium sites were identified as active sites in the reaction. This was further supported by a spectroscopic study that indicated that both univalent and trivalent rhodium took active part in the conversion [9]. Reduced rhodium was found inactive for methane activation. A more general summary concerning several catalytic metals (Rh, Pt, Ru, Pd and Ni) was made by Baerns et al. [50]. The mechanism deduced by Buyevskaya was generalized to include more materials than only rhodium. An important difference between pure metal catalysts and supported metal catalysts was proposed: Oxygen spillover from the support to the active metal sites. The importance of the water gas shift reaction during partial oxidation of methane over Pt/MgO was studied by Wolf and coworkers [51]. Water gas shift was found to be faster than reforming and thereby important for product distribution. This is also known to be the case during conventional steam reforming.

The study of platinum and rhodium catalyzed partial oxidation of methane conducted by Mallens and coworkers [52,53] concluded in a series-parallel mechanism similar to what was proposed by Hickman and coworkers [30-34]. Mallens proposed three different types of oxygen present on platinum surfaces [52]: Platinum oxide, dissolved oxygen and adsorbed oxygen. These three types yielded different products in oxidation reactions. Mallens also studied the rhodium catalyzed partial oxidation of methane [53]. It was found that rhodium gave a lower activation energy for methane activation than platinum and thus giving higher turnover rates. The selectivity to syngas with rhodium was also superior to platinum, and the results were explained in a similar way as was done previously by Hickman and Schmidt by the lower rate of hydroxyl formation on rhodium than on platinum. Mallens stated that carbon monoxide was formed directly as a primary product on rhodium as opposed to the conclusion made by Buyevskaya for steady-state operation [47,48].

Heitnes Hofstad also studied the rhodium catalyzed partial oxidation of methane in a TAP reactor [18]. Both pure rhodium sponge and supported Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was studied. This study also states that bulk oxygen participates in the conversion and that oxygen spillover can be significant with supported catalyst systems. The conclusion

concerning the formation of primary products in the study of Heitnes Hofstad is similar to the mechanism proposed by Hickman [30-34] and Mallens [53] but differ from the conclusion made by Buyevskaya [47,48].

These studies differ in conclusion concerning the primary products during the partial oxidation of methane on rhodium. Buyevskaya concluded that carbon dioxide was primary product whereas Hofstad and Mallens concluded that carbon monoxide and hydrogen were primary products. Hofstad also stated that oxygen spillover was important on supported rhodium catalysts. Buyevskaya states that the degree of reduction of the surface is crucial for the catalytic performance of the catalyst. The degree of reduction involves the coverage of oxygen. It is evident that different results can be obtained with different oxygen concentrations on the surface. The support can also influence the oxygen coverage by spillover. It is therefore possible that different conclusions can be made from results obtained from surfaces with different degree of oxidation.

Another possibility for the different conclusions in this context is the assumptions about a gradient-free catalyst bed in the TAP reactor. The interpretation of TAP response curves concerning primary products is further discussed in paper III and Chapter 4.2.

## **2.4 Methane partial oxidation by cerium oxide**

Oxygen storage capacity and oxygen transport dynamics in cerium oxide is well known and widely used industrially. In automotive exhaust catalysts cerium oxide acts as an oxygen reservoir supplying oxygen in short periods where the exhaust can be poor in oxygen [54]. Cerium oxide can also be used in dense solid oxide membranes for direct methane conversion fuel cells [55] or for electrochemical conversion of methane to syngas [56]. Cerium oxide is often modified with yttria or zirconia. Gas-solid reactions between methane and solid oxides have also been extensively studied in the past for application in the oxidative coupling of methane.

Studies of synthesis gas formation from the gas-solid reaction between methane and cerium oxide were first published by K. Otsuka and coworkers at the Tokyo Institute

of Technology in 1997 [57-59]. Physical mixing with platinum black drastically enhanced the conversion rate of methane. The oxygen dynamics of the cerium oxide phase was further improved by mixing zirconia into the cerium oxide phase by co-impregnation. It was found that the composition giving the best oxygen mobility was  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  [59]. However, a recent study indicates that addition of zirconia into the ceria can increase the production of carbon dioxide and water on behalf of the selectivity to synthesis gas [60]. This shows that there is a correlation between the selectivity to partial oxidation products and the oxygen mobility. If the mobility of oxygen becomes too good, it simply leads to more oxidized products.

### 2.5 Mechanistic studies in pulse reactors

Some of the results presented in this study are based on work in a near-atmospheric pressure pulse reactor. Other researchers [61-69] have also studied the mechanism of the partial oxidation of methane in catalytic pulse reactors at near-atmospheric pressures. The above-mentioned publications come from two laboratories; State University of New York (Hu, Ruckenstein and Wang) and Hong Kong Baptist University (Au and Wang).

Since only small amounts of reactant is injected in each pulse over the catalyst the reactor is near isothermal. The reactions of methane and oxygen with a solid material can be studied by separately pulsing methane and oxygen into the reactor. Thus, disturbing effects of gas phase oxidation can be avoided. Otherwise, mixtures of methane and oxygen can be pulsed into the reactor. The presence of gas phase oxygen may prevent carbon deposition on the solid material.

Hu and Ruckenstein [61-63] studied the partial oxidation of methane over supported Ni-catalysts in a pulse reactor. They proposed a mechanism where adsorbed methane was stepwise dehydrogenated on the reduced Ni metal and the carbon species was subsequently oxidized to carbon monoxide and carbon dioxide on the surface. Thus, hydrogen and carbon monoxide may be formed as primary products on a reduced Ni-catalyst. However, Wang and Au [64-66] proposed a very similar mechanism based on their pulse studies of methane oxidation with  $\text{Ni}/\text{SiO}_2$  that was published at exactly

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the same time (1995-1996) as the work of Hu and Ruckenstein. Au and Wang [67] came to a similar conclusion concerning Rh/SiO<sub>2</sub> catalysts. Wang and Ruckenstein [68,69] published more detailed studies of the effect of the support on rhodium catalyzed partial oxidation of methane. Strong metal-support interactions (SMSI) were found to have an influence on the reducibility of the rhodium and thereby also on the product formation and the activity of the catalyst. Fundamental differences between irreducible (ex.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO) and reducible support materials (ex. CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>) were also identified to be important. It was found that, in general, reducible-oxide-supported rhodium catalysts have much lower activity and selectivity than those supported on irreducible supports. Formation of mixed suboxides of rhodium was proposed as an explanation as it reduces the amount of active sites.

## 3 Experimental

### 3.1 Catalyst properties

#### 3.1.1 The noble metal gauze catalysts

The Pt and Pt/Rh gauze catalysts were supplied from K.A. Rasmussen, Hamar, Norway. The dimensions of the gauzes are given in Table 3.1 below.

Table 3.1: Gauze catalyst dimensions

<i>Gauze</i>	<i>Wire diameter</i>	<i>Mesh density (1/cm<sup>2</sup>)</i>
Pt	90 $\mu\text{m}$	256
Pt/5%Rh	60 $\mu\text{m}$	1024
Pt/10%Rh	60 $\mu\text{m}$	1024

#### 3.1.2 The promoted cerium oxide materials for the gas-solid reaction studies

The materials were prepared by incipient wetness impregnation of about 20% CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> material was supplied by Alfa Aesar in pellets and crushed down to particles in the size 300-710 $\mu\text{m}$ . The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with Ce(NO<sub>3</sub>)<sub>3</sub>\*6H<sub>2</sub>O dissolved in distilled water, dried at 150°C and calcined in air at 600°C for 10 h. The materials were reimpregnated with either 0.5wt% Pt (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) or Rh (Rh(NO<sub>3</sub>)<sub>3</sub>) and calcined again in air at 600°C for 10h. Detailed characterization (BET, XRD, H<sub>2</sub>-TPR) of the material samples was performed and is presented in paper IV. The surface area decreased from about 198 to 158m<sup>2</sup>/g by impregnation of 20wt.% CeO<sub>2</sub> on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

### 3.1.3 The ceramic cordierite monolith catalysts

The monolithic support structures were made from cordierite. The properties of the monoliths and washcoat used in this study are given below in Table 3.2.

Table 3.2: Properties of the ceramic monolithic support and the washcoat material.

Ceramic monolithic support structure		Washcoat	
Manufacturer	CORNING	CONDEA	
Product name	CELCOR 400/6.5	DISPERAL P2	
Cell geometry	Square	<i>Powder as delivered</i>	
Cell density	62.2 cells/cm <sup>2</sup>	Loose bulk density	0.86 g/ml
Wall thickness	0.16 mm	Particle size (d <sub>50</sub> )	45 μm
Hydraulic diameter	1.1 mm	Al <sub>2</sub> O <sub>3</sub> content	73%
Open area	76%	Na <sub>2</sub> O content	0.002%
Surface/volume	2790 m <sup>2</sup> /m <sup>3</sup>	NO <sub>3</sub> content	4.0%
Open porosity	33%	<i>Water dispersion (15wt%)</i>	
Mean pore size	3.5 μm	Dispersibility	98%
Thermal expansion coefficient	10*10 <sup>-7</sup> / °C (25-1000 °C)	Particle size	25 nm
Axial rupture strength	300 psi	<i>After activation at 550 °C for 3 hours</i>	
Melting point	1450 °C	Surface area (BET)	260 m <sup>2</sup> /g
Chemical composition	2MgO·2Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>	Pore volume	0.5 ml/g



## 3.2 Catalytic testing equipment

### 3.2.1 Short contact time continuous flow reactor

This apparatus was used for all short contact time steady flow experiments with the Pt and Pt/Rh gauzes for the partial oxidation of methane presented in papers I and II. It was also used in the study of the oxidative dehydrogenation of propane presented in paper V. The rig (Figure 3.1) was equipped with two separate feed lines. A four-way valve at the entrance of the reactor allowed manual switching between the lines. There was one bypass line in parallel with the reactor. One of the feed lines was used for pretreatment gas mixtures (hydrogen). The main feed line was used to feed hydrocarbons (mainly methane), oxygen and argon in total flow rates up to 2500 Nml/min.

The reactor used in the short contact time experiments (Figure 3.2 and 3.3) consisted of a quartz tube (i.d.=16mm). The catalysts were placed on top of a thick (o.d.=15mm, i.d.=4mm) quartz tube to minimize the downstream heated volume. A closed thin quartz tube (i.d.=3mm) in the center of the reactor allowed insertion of a thermocouple to any position through the reactor. The catalysts (gauze or coated monolith) were cut into pieces with a diameter of 15mm. A 3mm hole for the thermocouple was cut or drilled out of the monoliths. The catalyst was placed between two pieces of uncoated cordierite monoliths that were 10mm high and 15mm in diameter.

The quartz reactor was placed inside an electrical furnace. The temperature in the furnace was regulated with a separate thermocouple outside the quartz reactor. The electrical furnace could be heated up to 1000°C. The temperature inside the reactor could be as high as 1150°C, but these high temperatures only occurred on ignition and were never held for longer periods of time. Radiation complicates gas temperature measurements at these conditions. This is further discussed where relevant for the results. However, the thermocouple measured large temperature gradients inside the reactor. The contact time estimates in this reactor were therefore based on the feed flow at normal conditions (0 °C, 1.0 atm.) and the void volume in the catalyst. All experiments were conducted at atmospheric pressure and the pressure drop over the monolithic catalysts studied was negligible.

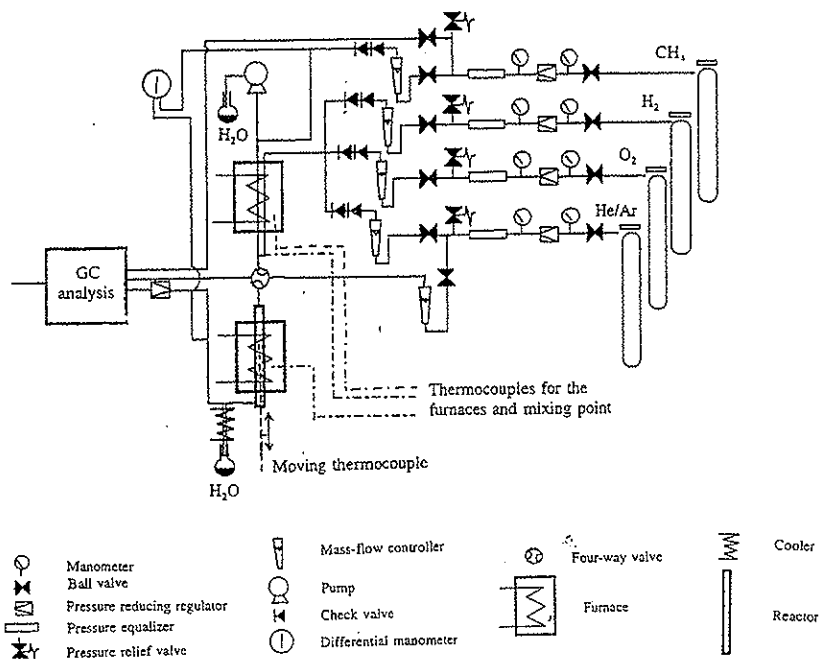


Figure 3.1: Short contact time steady flow reactor rig

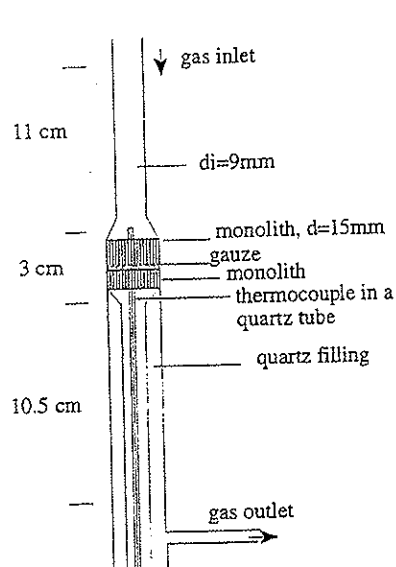


Figure 3.2: Reactor for gauze catalysts

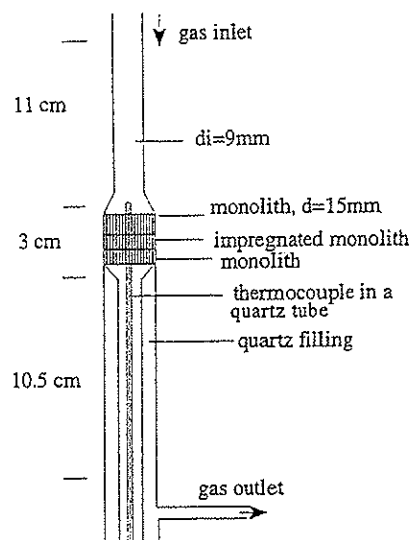


Figure 3.3: Reactor for ceramic monolith supported catalysts

Immediately downstream of the reactor there were two water-cooled condensers in series. A bleed flow of the dry product stream was taken to on-line gas chromatographic analysis. The analysis was conducted with two separate GCs. One HP 5890 with argon as carrier gas and one HP 5880 with helium as carrier gas. Three samples of the dry product gas were injected into separate columns with separate detectors. The temperatures in the GCs were slowly increased from 40 °C to 200 °C to ensure good separation. The details of the analysis are shown in Table 3.3.

Table 3.3: Details of the product analysis by gas chromatography

<i>Sample</i>	<i>GC</i>	<i>Carrier gas</i>	<i>Column</i>	<i>Detector</i>	<i>Components</i>
1	HP 5890	Argon	Capillary GS-Q 30m	Flame ionization	CH <sub>4</sub> , C2-C5
2			Packed Carboxen 1000 3 m	Thermal conductivity	H <sub>2</sub> , O <sub>2</sub> , (CO), CH <sub>4</sub>
3	HP 5880	Helium	Packed Carboxen 1000 3 m	Thermal conductivity	CO, CH <sub>4</sub> , CO <sub>2</sub>

Methane was detected with all three detectors and used to connect the areas. The conversion of methane was never above 50%. The material balance was not closed since water was condensed out of the product mixture before the analysis. The conversions and selectivities were calculated from the material balances. All areas were calculated as relative to methane to eliminate error from the injection valves.

### 3.2.2 High temperature TAP-2 multifunctional reactor

This setup was situated at the IRC-CNRS in Villeurbanne, France. The multifunctional TAP and TAP-2 reactors are thoroughly described in the literature [70,71]. Only a very brief presentation of the hardware setup with particular focus on the modifications for high temperature operation will be presented here.

The TAP-2 setup consists of three main sections. The largest part is the vacuum chamber containing the quadrupole mass spectrometer (UTI 100C). The vacuum is obtained by a mechanic pump, a 10 inch oil diffusion pump and an ionic pump. The whole chamber is cooled by liquid nitrogen. The normal background pressure in the vacuum chamber is approximately  $>10^{-8}$  torr ( $10^{-10}$  bar). The mass spectrometer is operated by a computer with special hardware and software that allows very rapid data acquisition. This provides very good time resolution and has given the name to the instrument: Temporal Analysis of Products (TAP). The mass spectrometer filament is situated at the top of the vacuum chamber close to a valve system that separates it from the reactor exit.

The reactor can be of different sizes, but consists generally of an electrically heated cylinder filled with the catalyst sandwiched between two layers of quartz particles. In the TAP-2 setup, the reactor exit is situated only a few cm above the mass spectrometer filament, leaving only enough space for the gate valve and the slide valve protecting the vacuum system. The most important difference between the old TAP and the newer TAP-2 setups is the distance between the catalyst where the reactions take place and the mass spectrometer. In the older TAP system, the distance between the reactor and the mass spectrometer was an order of magnitude greater.

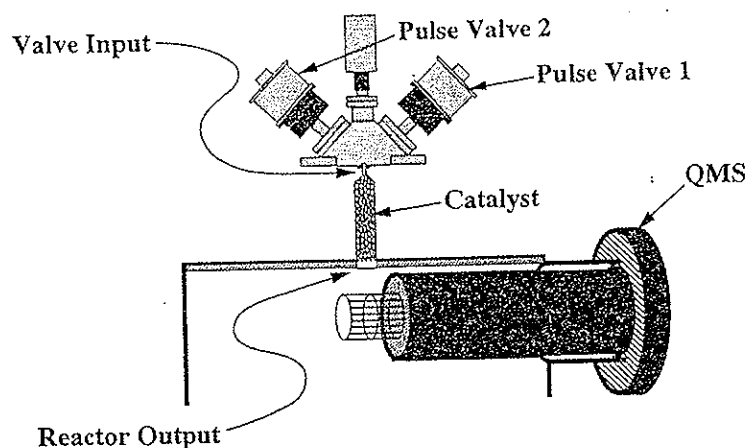


Figure 3.4: TAP-2 multifunctional reactor system

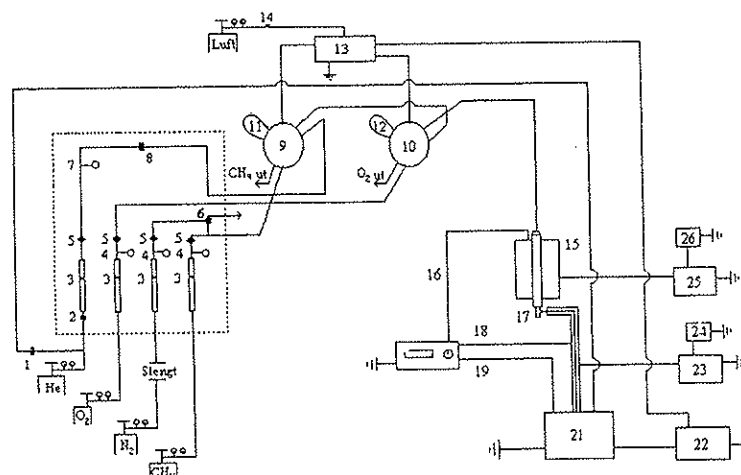
Located directly above the quartz reactor is the injection valve manifold. The manifold consists of four magnetically driven "jumping needle" valves. These valves have separate gas feed lines and can be operated separately. The injection valves consist briefly of a small hole in the zero-volume manifold plugged with a needle. A feed line exit close upstream of the hole gives an ambient pressure of the desired feed. The top of the evacuated reactor is immediately downstream of the hole. The needle that plugs the hole has a paramagnetic section surrounded by a conduction coil. An electrical pulse in the coil can cause the needle to jump slightly and a very small amount of the feed will slip through the hole into the top of the evacuated reactor. The magnitude of the electrical pulse determines the amount of gas that enters the reactor when the needle jumps. At normal conditions, the pulse size can be varied in the range between  $10^{13}$  and  $10^{20}$  molecules/pulse. The injected pulse of molecules moves downwards in the reactor by random walk Knudsen diffusion, through the catalyst bed where adsorption and surface reactions can take place and finally downwards and out to the quadrupole mass spectrometer that gives very good time-resolved outlet flow analysis.

Traditional TAP and TAP-2 setups are limited upwards in temperature at 600-750 °C. For the particular TAP-2 setup in Villeurbanne, the IRC-CNRS has developed new reactor/furnace equipment that allowed temperatures above 1000 °C. This reactor consists of a 9.0 cm long quartz tube with an inner diameter of 15 mm which is filled with quartz particles approximately 0.2 mm in size. Inside the quartz tube, the catalyst gauzes were situated floating horizontally in the quartz particles 4.5 cm above the reactor exit. A thermocouple inside the tube allowed temperature measurement at the exact position of the gauze. The quartz reactor was heated with an electrical external furnace surrounding the reactor tube.

### 3.2.3 Near-atmospheric pressure pulse apparatus

This apparatus was used for the experiments in paper IV. A schematic presentation of the apparatus is shown in Figure 3.5. The material/catalyst samples were placed inside a 3 mm diameter quartz tube heated inside an electrical furnace. A steady flow of helium (50 Nml/min) continuously flushed the material samples. Reactant pulses (0.25 ml = 10 micromoles) of methane, ethane, carbon dioxide or oxygen could be injected into the helium through two separate six-way valves. Downstream of the

reactor, all lines were thoroughly heated and the He flow proceeded directly into a packed Porapak Q column (2.1 m, ¼ inch) that was held isothermal at 70 °C. A TCD detector (and in certain cases a mass spectrometer) was placed at the exit of the packed column. The pressure drop over the column was approximately 0.8 bar at the given flow of helium leaving a total pressure of 1.8 bar in the reactor. This gave a linear gas velocity of 0.22 m/s at 700 °C (1.8 bar) and a contact time between the reactant gases and the material samples (0.5g sample, 0.5 g/ml, void fraction 0.4) of about 0.26 seconds. Complete separation and analysis (12-15 minutes) of the products from a reactant pulse was allowed before a new pulse was introduced. The materials were mostly studied in cycles of multiple pulses of oxygen and subsequently multiple pulses of methane (or ethane). Reoxidation of the materials could be done with a new series of either oxygen or carbon dioxide. Carbon accumulation was estimated both from material balances and by measuring the formation of carbon oxides while pulsing oxygen over the used samples.



- |    |                                    |    |                             |
|----|------------------------------------|----|-----------------------------|
| 4  | Manometers                         | 11 | Methane feed pulse loop     |
| 5  | Needle valves                      | 12 | Oxygen feed pulse loop      |
| 7  | Helium feed line                   | 15 | Electrically heated furnace |
| 9  | Pneumatically driven six-way valve | 17 | Quartz reactor              |
| 10 | Pneumatically driven six-way valve | 21 | Gas chromatograph           |

Figure 3.5: Near-atmospheric pressure pulse apparatus.

## 4 Results

This section is a summary of the results obtained in papers I-V. The study presented in paper III was conducted at the IRC-CNRS in Villeurbanne, France.

### 4.1 Short contact time catalytic partial oxidation of methane (Papers I and II)

This study was a direct continuation of the work done by K.H. Hofstad [14-19]. The experimental setup and the details of the catalysts are described in Chapter 3.1 and 3.2. Short contact time partial oxidation of methane was considered important in order to obtain information about the initial reaction steps and the role of a noble metal catalyst.

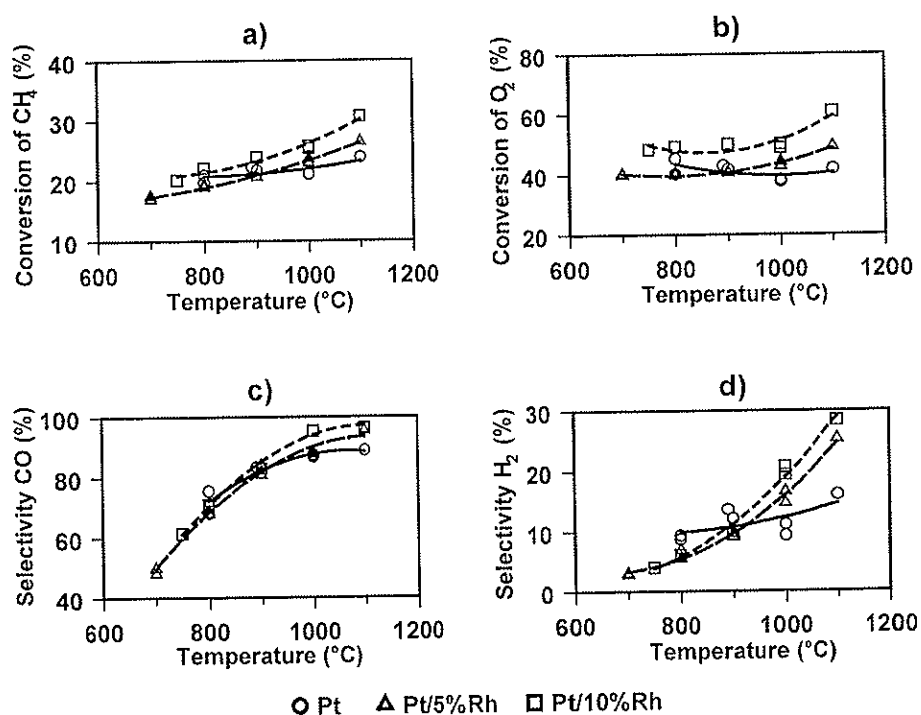
The Pt/Rh gauzes are presently used industrially in the ammonia oxidation process and in the Andrussov HCN process. Rhodium is in these processes found to have effect on the time on stream stability of the gauze catalysts.

The stability and activity of the Pt, Pt/Ir, Pd and Pt/Rh gauzes were compared for the catalytic partial oxidation of methane. It was found that pure Pt, Pt/Ir and pure Pd gauzes suffer from metal loss when exposed to the reaction conditions applied during partial oxidation of methane. The temperature on the ceramic monolith piece downstream of the gauzes increased with time on stream. This was always accompanied by a decrease in syngas selectivity. Noble metal volatilization and migration caused secondary combustion reactions to take place. The Pt/Rh gauzes were the only gauzes that showed fairly good stability at true reaction conditions. No temperature increase downstream of the gauze was observed with a Pt/10%Rh gauze catalyst at 900 °C over a time range of 8 hours. Alloying the platinum with rhodium was therefore found to be beneficial for preventing platinum volatilization.

There were also effects of rhodium on the gauze catalytic activity and selectivity for the conversion of methane. Figure 4.1 shows conversions and selectivities at identical reaction conditions over a single layer of Pt, Pt/5%Rh or Pt/10%Rh gauze catalysts. The flow rate was high and the contact time with the gauze was approximately 0.2

ms. The temperature on the axis in Figure 4.1 was measured at the exact position of the gauze catalyst. The external furnace temperature was used to regulate the gauze temperature. Results that have been published from other groups [31,34,46] are in good agreement with these data.

The figure clearly shows that the conversion of methane is rather low (15-30%) over the large range of temperatures from 700 to 1100 °C. The conversion of oxygen is higher, but remains incomplete (<60%) at all catalyst temperatures with this extremely short contact time. The selectivities to hydrogen and carbon monoxide are most strongly affected by the gauze temperature. The selectivity to carbon monoxide becomes high at about 1000-1100 °C, but the selectivity to hydrogen remains below 30% even at a gauze temperature of 1100 °C.



*Figure 4.1: Influence of gauze temperature on conversion and selectivity over Pt and Pt/Rh gauzes. The total feed flow is 2000 Nml/min and the CH<sub>4</sub>:O<sub>2</sub>:Ar ratio is 2:1:10.*



The effect of rhodium is positive for the conversion of both reactants and the selectivity to both carbon monoxide and hydrogen. The low increase in both methane and oxygen conversion as function of temperature is in good agreement with the transport limitations proposed in the literature [30,46]. The effect of various parameters on the catalytic stability, activity and selectivity of the noble metal gauzes was thoroughly studied.

The mechanism of syngas formation and the reaction pattern was further studied by analyzing the effect of co-feeding water and by studying the effect of increasing the contact time. Water takes part in several possible reactions both as a combustion product (E3), as a methane reforming reactant (E4) and in the water-gas shift (WGS). Co-feeding water with the methane and oxygen was therefore expected to give information about the extent of the above-mentioned secondary reactions involving water. An experiment was conducted at steady-state conditions with a feed of methane, oxygen and inert. The contact time was 0.2 ms as in the previous experiments. At a certain time some of the inert was replaced by water. The result showed that there was no significant effect on neither of the reactant conversions nor on the product selectivities. Water can therefore be considered as an inert at these short contact time conditions.

This experiment had rather important consequences for the kinetic understanding of the processes involved: Neither steam methane reforming (E4) nor water-gas shift (E4-E5) have a significant effect on the product formation at such short contact times. The formation of carbon monoxide and hydrogen must therefore be ascribed to the primary oxidation of methane (E1). The formation of carbon dioxide and water proceed through the secondary oxidation steps E2 and E3. The experimentally observed main products at high temperatures were water and carbon monoxide. The formation of carbon dioxide was only significant at low temperatures. This behavior could appear to be a result of water-gas shift equilibrium. The above experiment excluding water-gas shift therefore shows that the formation of these products is caused by kinetics rather than thermodynamics. The combustion of hydrogen (E3) appears to be more rapid than combustion of carbon monoxide (E2), especially at high temperatures

At incomplete conversions of both methane and oxygen, an increase in the contact time between the reactant gases and the catalyst should allow the dominating processes to proceed even further and finally possibly show influence of secondary reactions. Figures 4.2a and b show the effect of contact time on the conversion and selectivities from methane and oxygen over a Pt/5%Rh gauze at 1050 °C. This experiment was done isothermally with a constant gauze temperature. The external furnace temperature was increased with increasing contact time in order to maintain the same catalyst gauze temperature.

The experiment with co-feeding water at a contact time of 0.2 ms indicated that only primary reactions (E1, E2 and E3) take place at the extreme left of Figures 4.2a and b. The product formation at these conditions appears to be controlled by mass transport limitations and the relative rates of the different oxidation processes.

Figure 4.2a shows that the conversion of oxygen increased much more rapidly than the conversion of methane. The conversion of oxygen reached 100% at a contact time of about 3 ms. The conversion of methane continued to increase towards 45% at a contact time of 5.4 ms. The selectivities show very good agreement with what could be predicted from the previous experiments. At very low contact times, the selectivity to hydrogen decreases rapidly towards zero as would be expected from hydrogen combustion with oxygen. The selectivity to hydrogen thereafter remained low until the conversion of oxygen was complete. At very high contact times the selectivity to hydrogen again started to increase. The selectivity to carbon monoxide remained high and showed no clear increase until the conversion of oxygen was complete. This is all in very good agreement with the statement above concerning relative rates of hydrogen and carbon monoxide combustion. In addition, this experiment also shows that hydrogen combustion is more rapid than methane oxidation (E1). The conversion of methane increased very slowly as opposed to the very steep decrease in the selectivity to hydrogen at the shortest contact times. The product distribution is as from partial combustion (E1+2\*E3) until the conversion of oxygen becomes complete. Thereafter the hydrogen selectivity started to become significant and must be formed by secondary methane reforming processes since the conversion of oxygen was complete.

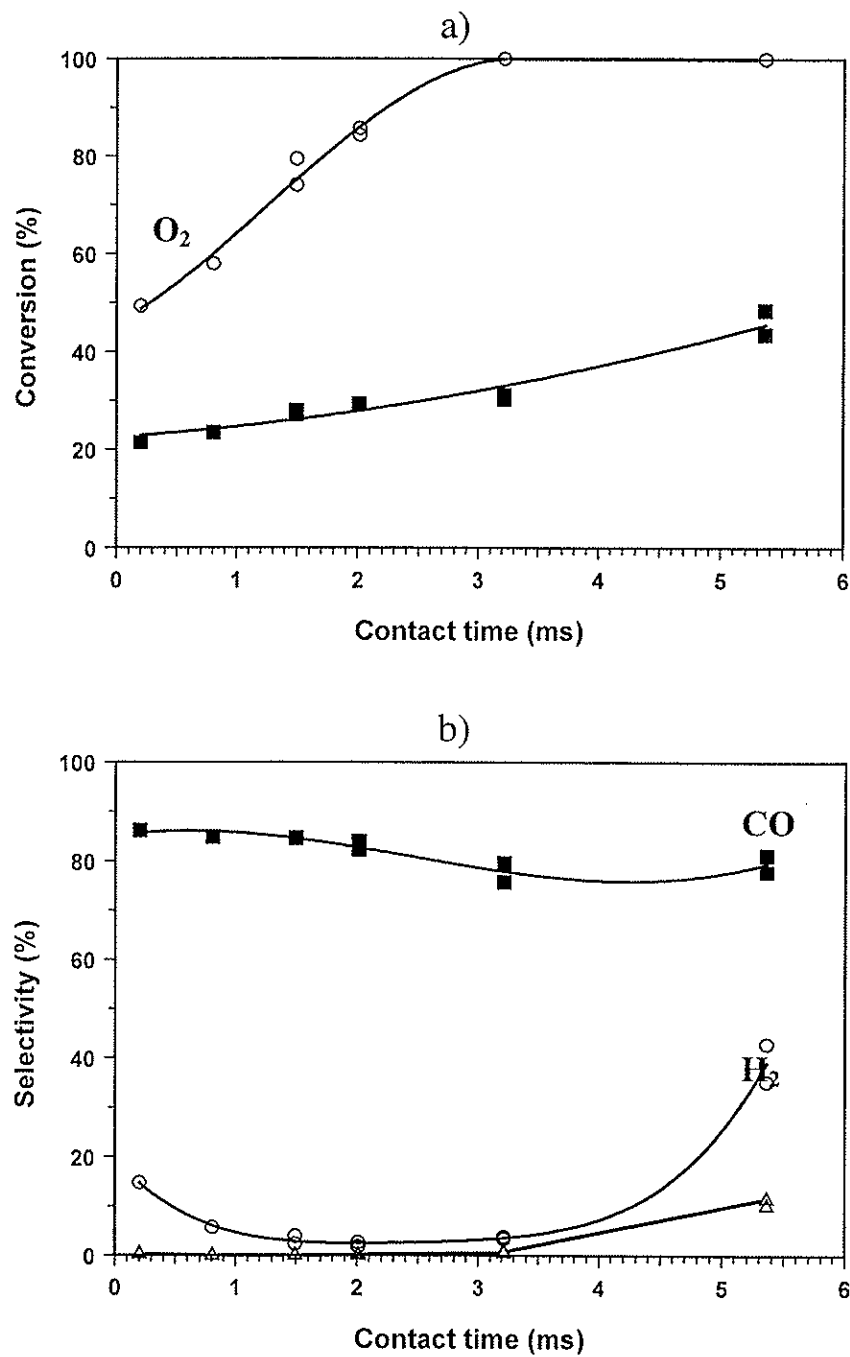


Figure 4.2: Conversion and selectivity over Pt/5%Rh gauzes at 1000 °C at various contact times. The feed composition is constant:  $\text{CH}_4:\text{O}_2:\text{Ar} = 2:1:4$ .

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One general conclusion can be deduced from the above experiments: The platinum catalyzed direct partial oxidation of methane with gaseous oxygen is a process where the products are more reactive than the reactant. This gives not only practical, but even theoretical yield limitations.

Equilibrated synthesis gas can obviously be formed through the reforming processes at high contact times, but this would be equivalent to what is done in commercially available ATR reactors where thermodynamics control the product distribution. The methane partial oxidation process (E1) is still the overall process equation without representing the actual chemistry that takes place. In ATR reactors, oxidation processes convert a maximum of only 33% of the methane even though the partial oxidation process (E1) is the overall reaction equation.

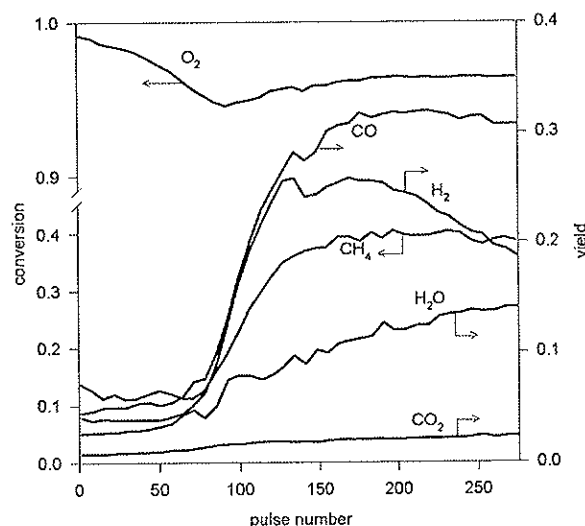
The reactivity of surface oxygen towards oxidation of the various reactants and products was identified as the key parameter for further studies.

## 4.2 The formation of primary products on platinum surfaces

### (Paper III)

The TAP-2 reactor was found to be particularly suited for such studies for several reasons: Firstly, no homogeneous processes take place at low pressures in the Knudsen diffusion regime, as is the case in the TAP reactor. This makes it possible to study heterogeneous processes without being influenced by homogeneous processes. Secondly, the reactions involved are very rapid. The TAP analytical tools enable very rapid data collection and provide information that cannot be obtained in conventional setups. This particular TAP-2 reactor also had the advantage of being equipped with a new high temperature furnace that enabled temperatures up to 1100 °C. All relevant TAP studies presented in the literature have been limited upwards in temperature to 750 °C. This is very low compared to realistic reaction conditions during steady-state catalytic methane partial oxidation. In addition, the gauze catalysts provide better information than particle/powder catalysts because they give a particularly thin catalytic zone. Axial surface concentration gradients can severely complicate the interpretation of TAP data. This can be a problem if the reactants have high sticking probabilities and if the reactions involved are rapid. At low temperatures, concentration gradients are not considered to be a problem in the TAP reactor because the sticking probabilities of the reactants are low. But at the extreme conditions used in this study (<1000 °C), the possibility of gradients is considerable. The platinum gauze used in this study had a wire diameter of 90  $\mu\text{m}$ . This extremely thin catalytic zone reduces the likeliness of surface concentration gradients.

One single layer of platinum gauze was estimated to have approximately 10 nmoles of surface platinum atoms. This number is lower than the amount of molecules in a TAP pulse (20-60 nmol). This constitutes a fundamental difference from all previous studies reported in the literature and is very important to keep in mind when interpreting the data. Full conversion of an oxygen pulse could easily be obtained with one single layer of platinum gauze. High conversion is an indication of high sticking probability and can result in axial surface concentration gradients. Addition of more catalyst would increase the amount of surface atoms, but this would also make gradients more likely.



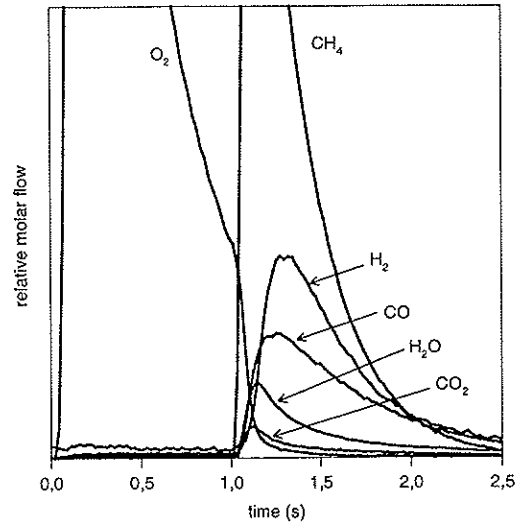
**Figure 4.3:** Conversions and yields as function of the pulse number over a prerduced platinum gauze at 1000 °C. Each pulse consisted of a mixture of methane, oxygen and argon.

The gauzes were initially prerduced in a steady flow of hydrogen at 900 °C. Figure 4.3 shows the conversions and yields when pulsing a mixture of methane and oxygen over a prerduced platinum gauze at 900 °C. In the first pulses, all the oxygen was accumulated on/in the catalyst and the conversion of methane was low. After a certain amount of pulses, the conversion of methane increased together with the formation of gaseous products. This showed that a large amount of oxygen was taken up by the bulk of the platinum before the actual conversion of methane with oxygen started to take place. As a consequence of this, all catalysts were preoxidized prior to experiments involving methane. When pure oxygen was pulsed over a prerduced catalyst, all the oxygen in the first pulses was absorbed. After a certain amount of pulses, oxygen started to break through and the catalyst sample gradually became saturated. The platinum catalyst absorbed far more oxygen than what could be explained by surface adsorption. The amount of oxygen taken up by the platinum in such a pretreatment corresponded to approximately 26000 monolayers. Hence, a working platinum catalyst at these conditions holds oxygen also in the bulk of the platinum. The active sites on the surface of a heterogeneous catalyst are generally

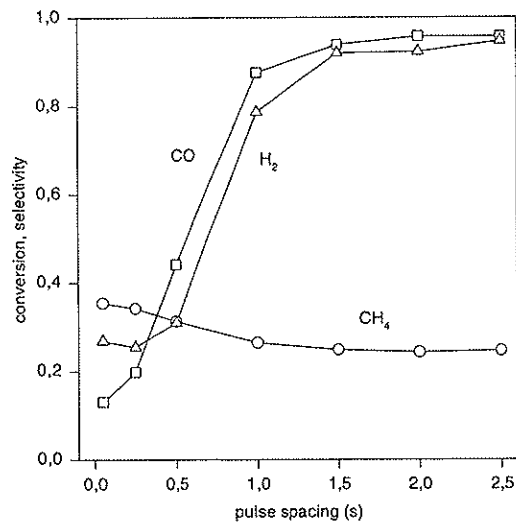
assumed to be supplied by reactants by gas phase adsorption. However, the fact that the working platinum catalyst held large quantities oxygen below the surface implied that, in this particular case, the active sites on the surface could be supplied with oxygen both by diffusion from the bulk and by adsorption from the gas phase. The relative rates and importance of these processes were further studied in detail. It was found to be of particular interest to study the correlation between how oxygen is supplied to the active sites and how this affects the selectivity and activity to form the various oxidation products.

All pulse sizes in this study corresponded to a number of molecules per pulse larger than the amount of surface atoms. The surface coverages of the reactants therefore changed during the time a reactant pulse diffused through the reactor. Alternating pulse experiments were conducted with injection of oxygen at one point in time followed by injection of methane at a certain point in time later ( $<2.5\text{s}$ ). The time between the oxygen and methane injections is referred to as the pulse spacing. The surface coverage of oxygen on the preoxidized platinum gauze was found to be low under vacuum conditions. The concentration of oxygen in the bulk of the platinum could be considered constant within the time scale of such experiments. During the oxygen pulse flow through the reactor, the oxygen coverage on the platinum catalyst surface increased and decreased again as function of the oxygen pressure at the position of the gauze. The methane pulse followed the oxygen pulse with various pulse spacings. Varying the pulse spacing was in this case therefore the same as varying the initial oxygen coverage on the platinum surface at the time when methane reached the position of the gauze. Figure 4.4 shows the reactant and product responses during an alternating pulse experiment with a pulse spacing of 1.0 second. The surface concentration of oxygen on the platinum rapidly dropped towards zero when the methane pulse reached the gauze and removed oxygen by reaction.

Figure 4.4 shows that the formation of the various oxidation products changed drastically during the time ( $>0.5\text{s}$ ) that the gauze was exposed to methane. Water and carbon dioxide were formed from the first methane molecules that arrived at the platinum surface while the concentration of oxygen was still high. The formation of these products disappeared rapidly as the surface oxygen was being removed.



*Figure 4.4: Transient responses of reactants and products during an alternating  $O_2$ - $CH_4$  pulse experiment over a preoxidized Pt-gauze at  $900^\circ C$  with a pulse spacing of 1.0 s.*



*Figure 4.5: Conversion of methane and selectivity to synthesis gas from an alternating pulse experiment over a preoxidized platinum gauze at  $900^\circ C$  with oxygen injection at time zero and methane injection at the time indicated by the pulse spacing.*



The formation of hydrogen and carbon monoxide continued even after most of the methane had come out of the reactor. Carbon dioxide reforming of methane was found not to take place. Figure 4.4 therefore shows very clearly that there is no absolute universal answer to what are the primary products from methane oxidation over platinum. Carbon dioxide and water are formed as primary products when the surface is rich in oxygen whereas carbon monoxide and hydrogen are primary products when the surface concentration of oxygen is low. The oxygen coverage is the most important parameter for the primary product formation. Figure 4.4 also shows that one can not make conclusions based simply on what comes first out of the reactor when the surface concentrations are not constant. The above results are in good agreement with a very simple model of the reaction pattern based on consecutive oxidation of carbon:

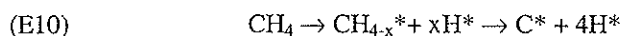


Figure 4.5 shows how the overall methane conversion and syngas selectivity varied with the pulse spacing. Extremely high selectivities to carbon monoxide and hydrogen were observed at high pulse spacing (>2s) when methane reacted with oxygen solely diffusing to the surface from the bulk. The conversion of methane decreased from about 35% in reaction with gas phase oxygen to about 25% in absence of gas phase oxygen. A decrease in methane conversion from 35% to 25% was in fact not as much as might be expected given the different nature of the catalytic gas-gas reaction at the short pulse spacings and the gas-solid reaction at the highest pulse spacings. Figure 4.5 shows very nicely the effect of removing gas phase oxygen during oxidation of methane over platinum.

Another similar experiment was conducted with alternating pulses of methane and  $^{18}\text{O}_2$  over platinum that had been preoxidized in  $^{16}\text{O}_2$ . This made it possible to distinguish between reactions with oxygen adsorbing from the gas phase and oxygen

diffusing through the solid platinum. A schematic illustration of how this experiment was assumed to proceed is shown in Figure 4.6.

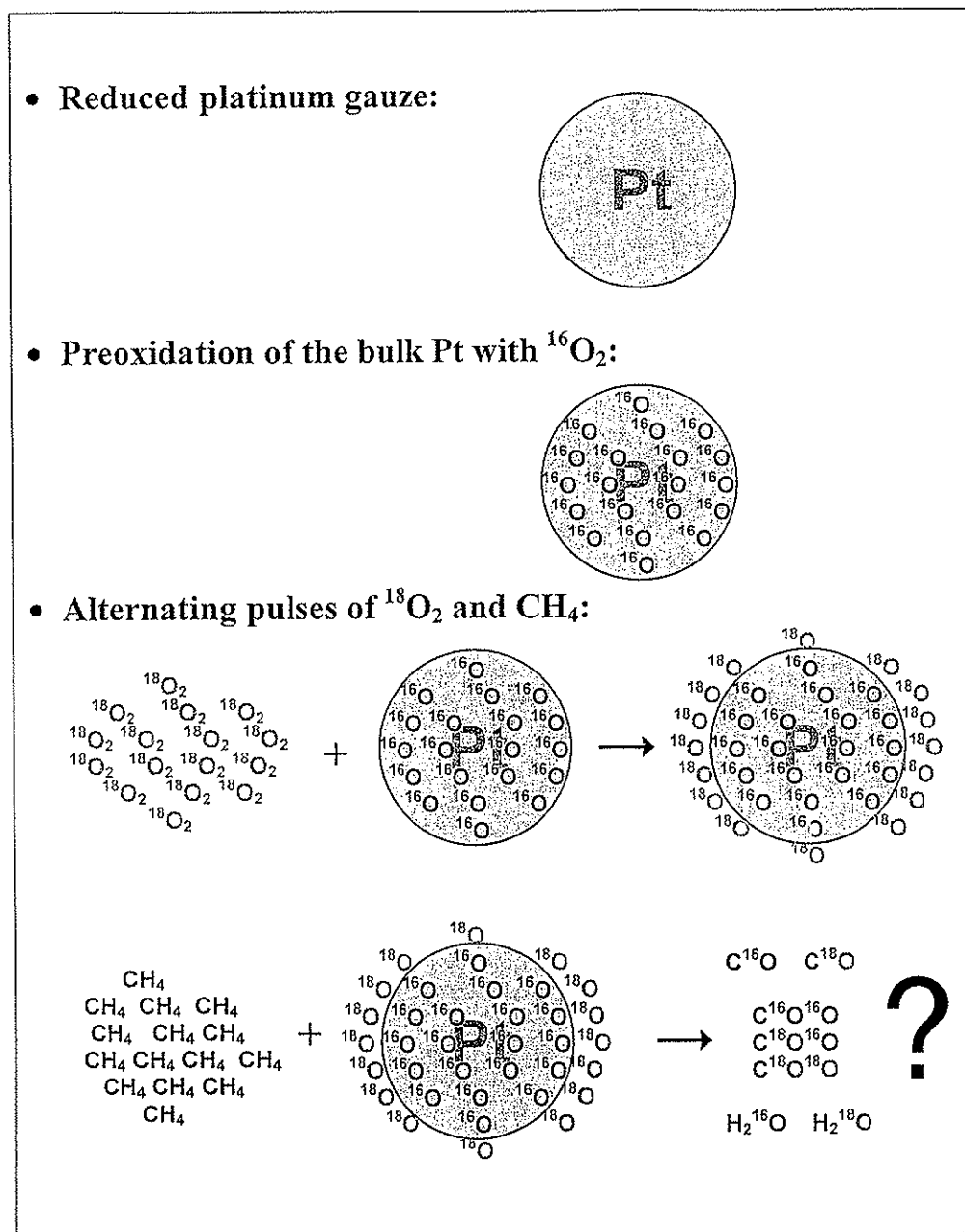
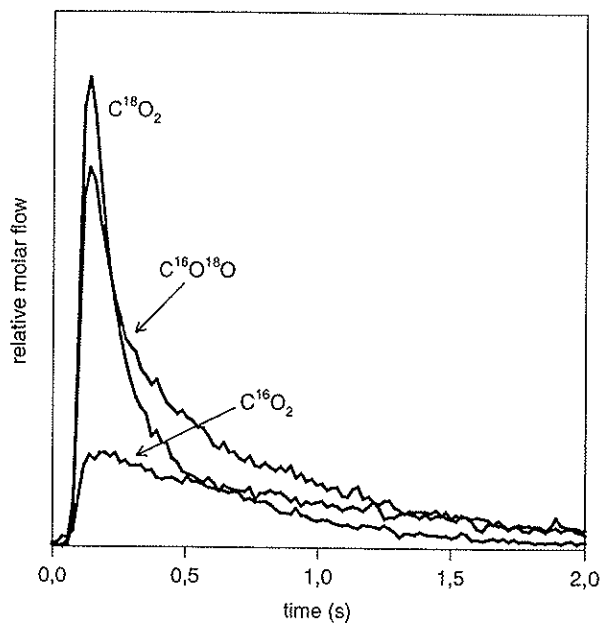
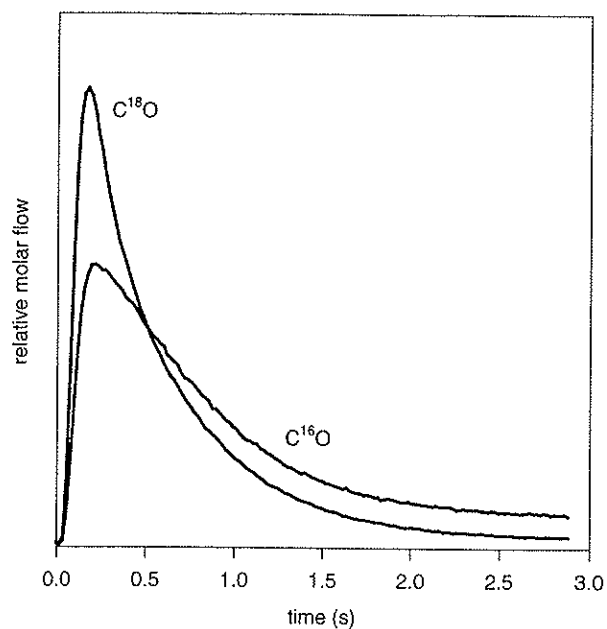


Figure 4.6: Illustration of an experiment with alternating pulses of labeled oxygen and methane over a preoxidized platinum gauze.



*Figure 4.7: Transient responses of carbon monoxide (upper figure) and carbon dioxide (lower figure) in an alternating pulse experiment with  $^{18}O_2$  (g), methane and  $^{16}O_2$ -preoxidized platinum at 900 °C. The time is relative to the injection of methane.*

This experiment provided very interesting information about which products were formed from the different oxygen supply routes. Information about the relative rates of some of the different processes taking place could also be derived from the results.

As seen from Figure 4.7, the transient response of  $C^{16}O$  was largely different from the response of  $C^{18}O$ . The  $C^{16}O$  response was clearly delayed and tailed and this was used to estimate the rate of oxygen diffusion in platinum. Figure 4.7 also shows that there were indeed large differences in the responses of  $C^{16}O_2$ ,  $C^{16}O^{18}O$  and  $C^{18}O_2$ . One clear general trend is that molecules containing  $^{18}O$  have markedly sharper response curves than the molecules containing  $^{16}O$ . The formation of products from  $^{18}O$  supplied from the gas phase was very rapid and the diffusion of  $^{16}O$  from the bulk to the surface delayed the formation of these products.

The distribution of the two oxygen isotopes within carbon monoxide and carbon dioxide also varied with the pulse spacing. As could be expected, the amount of  $^{16}O$  increased and the amount of  $^{18}O$  decreased with increasing pulse spacing. Figure 4.7 shows that very little  $C^{16}O_2$  was formed compared to the other carbon dioxides. This was the case at all pulse spacings where carbon dioxide was observed. The amounts formed of  $C^{18}O_2$  and  $C^{16}O^{18}O$  were not significantly different. This shows very clearly that the diffusion of oxygen in solid platinum was too slow to double-oxidize carbon. The first oxidation of carbon to carbon monoxide could almost equally well be by bulk diffusion of  $^{16}O$  as by  $^{18}O$  adsorbed from the gas phase. However, the second oxidation appeared to be almost exclusively with  $^{18}O$ .

Analysis of the water formation from the different oxygen isotopes was unfortunately impossible. There were severe disturbances on A.M.U. 18 ( $H_2^{16}O$ ) from the above mentioned carbon monoxide and carbon dioxide isotopes coming out of the reactor at different times.

The rate of oxygen diffusion in solid platinum was quantified and found considerably slower than the rate of carbon monoxide desorption. This was proposed to be the reason for the extremely high selectivity to carbon monoxide in the absence of gas phase oxygen. When the rate of oxygen supply to the surface is slower than the rate of

desorption of the reaction intermediate, a logical consequence is that the probability of consecutive oxidation to carbon dioxide is very low. The high selectivity to hydrogen was explained similarly and correlated to the surface residence time of hydrogen. The only syngas component that showed high activity to reducing the preoxidized platinum was methane. This was proposed related to the irreversible nature of methane adsorption. Methane decomposition to carbon and hydrogen leaves carbon on the surface with an infinite surface lifetime unless it is gasified by one or two adsorbed oxygen species. Whether it is one or two depends on the ratio between the surface residence time of carbon monoxide and the rate of oxygen supply.

This study therefore concluded with that carbon monoxide and hydrogen are primary products from platinum catalyzed partial oxidation of methane when the surface concentration of oxygen is low. If the oxygen supply to the surface is constrained, the selectivity to syngas can be very high. This can be done by supplying oxygen to the active sites by solid diffusion instead of by adsorption from the gas phase.

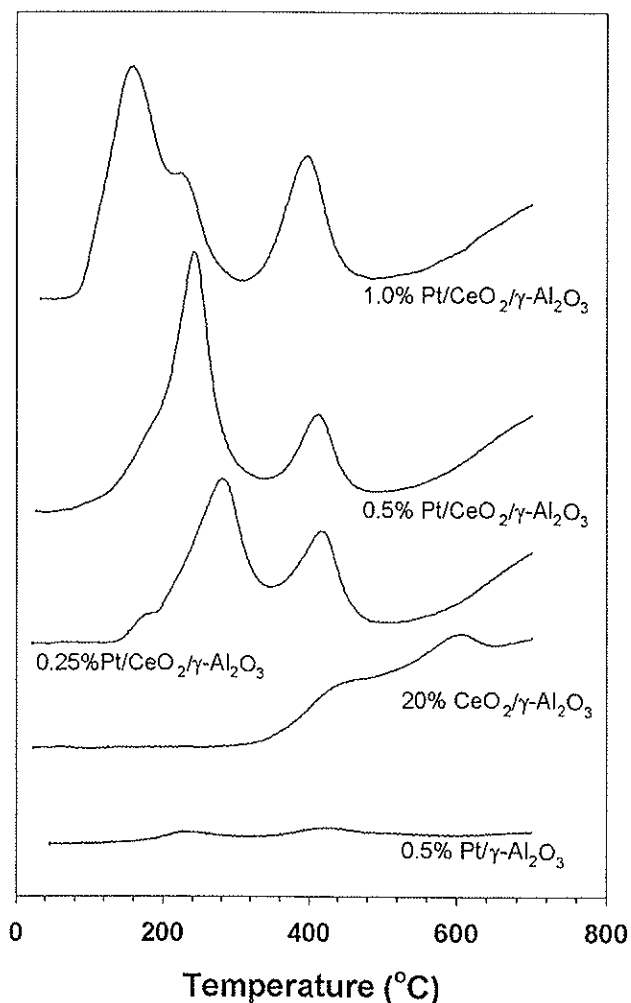
### 4.3 Methane oxidation by promoted cerium oxide (Papers IV and V)

It was shown in Chapter 4.2 that methane could form carbon monoxide and hydrogen with high selectivity in the reaction with oxidized platinum. The oxygen supply to the active site could be constrained by feeding the oxygen through solid diffusion rather than by gas phase adsorption. The overall reaction rate was lower in absence of gas phase oxygen, but a relative decrease in conversion from 35% to 25% was not as discouraging as one could expect.

As described in Chapter 2.3, cerium oxide is a good dynamic oxygen reservoir. A three-component solid material was prepared for further studying the gas solid reaction between methane and solid bound oxygen. The object was to make syngas at low temperatures with high selectivity and productivity. High surface area was considered to be important in order to obtain good contact between the reactant gases and the solid oxygen carrier. A high-surface area support made from  $\gamma\text{-Al}_2\text{O}_3$  was impregnated with 20 wt%  $\text{CeO}_2$ . The addition of as much as 20 wt%  $\text{CeO}_2$  decreased the surface area of the support from about  $198\text{ m}^2/\text{g}$  to about  $158\text{ m}^2/\text{g}$ . Small amounts of platinum were finally impregnated on top of the two oxides to form the three-component material  $\text{Pt/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . High surface area was provided by the alumina. A large oxygen storage capacity was provided by the ceria and the capability to activate methane and slowly transport oxygen to the active sites was provided by the platinum. A detailed description of the preparation procedure together with the characterization data (XRD, TPR, BET) are shown in appendix IV (paper IV). Reference samples without platinum were also extensively studied in order to isolate the effect of platinum.

Temperature programmed reduction with hydrogen showed that platinum largely affected the reduction of the cerium oxide (ceria) phase. Figure 4.8 shows very clearly that the temperature necessary for reduction of the cerium oxide decreases when platinum is present on the ceria.

Reduction of cerium oxide by methane was studied in the near-atmospheric pressure pulse apparatus described in Chapter 3.2.3. Repeated pulses of reactants were injected into a constant flow of helium flushing the material sample.



*Figure 4.8: Temperature programmed reduction of various material samples: 0.5 wt%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 20 wt% CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.25-1.0 wt% Pt/CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.*

Very low conversion of methane was obtained with a CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample that had not been promoted by platinum. Tetravalent cerium (as in CeO<sub>2</sub>) has been reported also in the literature [58] to have very poor activity for methane activation. The addition of platinum by impregnation drastically enhanced the activity for methane conversion with cerium oxide. Figure 4.9 shows the product yields as methane was

pulsed over preoxidized 0.5wt% Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Bar charts were chosen to represent the results since they describe well the material balance and the discrete nature of the pulse experiments. The figure clearly shows that carbon dioxide and water were formed from methane reacting with fresh cerium oxide, but the product distribution changes towards carbon monoxide and hydrogen as the cerium oxide was being more and more reduced. The results also show that carbon deposits were accumulated on the material sample after a certain amount of oxygen had been removed. The hydrogen balance also indicates some hydrogen accumulation on the sample since almost no hydrogen containing molecules come off the sample in the first pulse. Hydroxyl formation on cerium oxide surfaces was suggested as a possible cause for hydrogen accumulation. After a few pulses, the selectivity to hydrogen was surprisingly high considering that this experiment was conducted at only 700 °C, which is very low compared to conventional hydrogen production processes. After the treatment as shown in Figure 4.9, the oxygen removal from the sample corresponded with a stoichiometric reduction of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub>. This experiment showed that there is a possibility to produce high purity syngas at low temperatures. The undesired initial formation of carbon dioxide diminished after injection of about 4 methane pulses. The methane slip occurred after 13 pulses. During the pulses from no. 5 through 13, pure synthesis gas was produced together with carbon accumulation on the material sample. It will be shown below that these carbon deposits selectively could be gasified to carbon monoxide and thereby providing high carbon efficiency.

Further experiments were carried out to get an idea of the mechanism of product formation in this system. The contact time in this particular setup with a material loading of 0.5 g was about 0.26s (700 °C, 1.8 bar). This contact time is very high compared to the short contact times (<1ms) obtained with the gauze catalysts in Chapter 4.1 and 4.2. Occurrence of consecutive reactions was therefore considered to be very likely in this particular case.



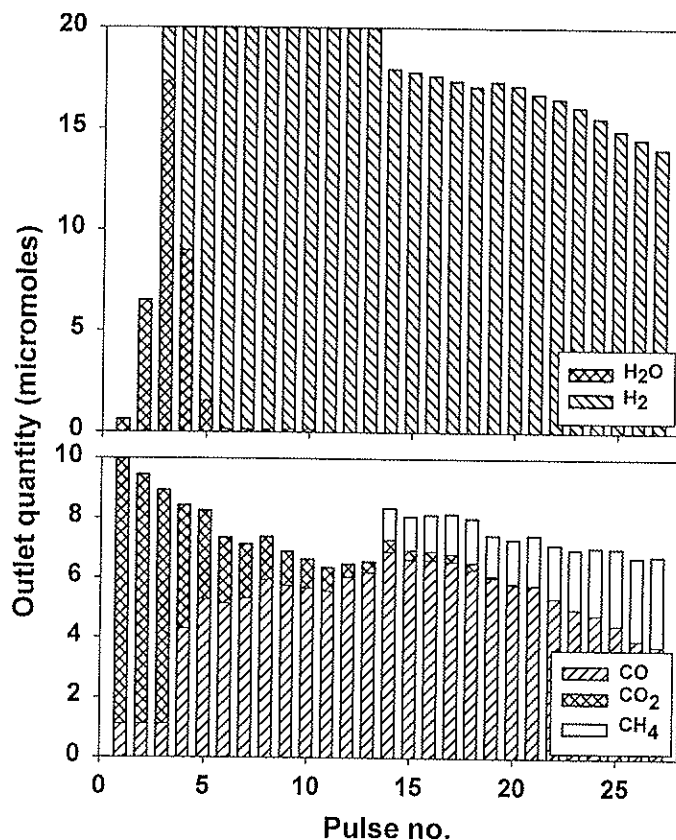


Figure 4.9: Product yields from pulsing methane (10 micromoles/pulse) over a preoxidized sample (0.5g) of 0.5 wt% Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at 700 °C. The products were analyzed by GC and MS.

A decrease in material loading in the reactor was expected to give higher selectivity to the products that were formed in the upper parts of the material bed and lower selectivity to the products formed by consecutive reactions further down in the bed. Similar experiments as the one presented in Figure 4.9 with 0.50g Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were performed with 0.25 and 0.125g of Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in the reactor. Table 4.1 shows the conversion of methane and the product selectivities from the first methane pulses over fresh material samples as function of the material weight loading in the reactor. The product selectivities from the first pulse of methane clearly changed towards more carbon monoxide and less carbon dioxide as the material weight

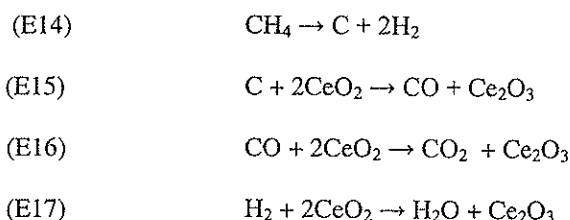
loading was decreased. There is a dramatic change in the selectivities when the conversion of methane decreases from 100%. As expected, this occurred earlier with decreasing weight loading. Hydrogen accumulation made a similar analysis difficult for hydrogen and water.

Table 4.1: Conversion ( $X$ ) and selectivity ( $S$ ) during methane pulsing ( $10 \mu\text{mol/pulse}$ ) over different amounts of  $0.5 \text{ wt\% Pt/CeO}_2/\gamma\text{-Al}_2\text{O}_3$  at  $700 \text{ }^\circ\text{C}$ .

<i>Material loading</i>	<i>Pulse number</i>	$X_{\text{CH}_4}$	$S_{\text{CO}}$	$S_{\text{CO}_2}$	$S_{\text{coke}}$
0.5 g	1	100%	10%	90%	-
	2	100%	10%	85%	5%
	3	100%	10%	80%	10%
0.25 g	1	100%	5%	95%	-
	2	100%	75%	20%	5%
	3	90%	90%	10%	-
0.125 g	1	100%	42%	53%	5%
	2	85%	93%	7%	-
	3	80%	97%	2%	1%

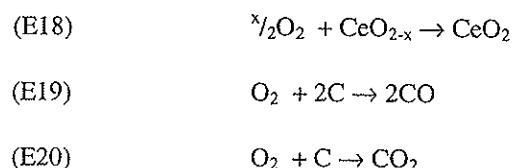
These experiments indeed gave indications that carbon monoxide was formed as a primary product at the top of the bed. However, the above experiments also showed that there had to be large axial gradients in the reactor. Full conversion of methane is also evidently a clear gradient indicator. The state of the solid cerium oxide as well as the surface concentration of oxygen could therefore not be constant throughout the whole material bed. Methane reached the bed from the top and gradually reduced the sample downwards as the oxygen was being removed. Reactive products such as carbon monoxide and hydrogen could also remove oxygen and be oxidized further down in the bed if they were formed at the top. The above experiments indeed shows that there were large axial gradients both in the gas phase concentrations and in the state of the solid material. There is therefore no universal nature of the primary products from the oxidation of methane in this gas solid reaction with high contact times and full conversions. The equations below (E14-E17) describe the reduction of cerium oxide with methane. Reaction E14 is strongly enhanced by the presence of platinum and all the results indicate that this occurs on the platinum surface. Since

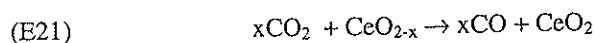
methane is activated on the surface of the platinum and the oxygen is supplied from the cerium oxide, E15-E17 represent more the overall process and not the actual chemistry. The oxidation of carbon is written as two consecutive reactions, E15 and E16. Consecutive oxidation includes the possibility of both carbon monoxide and dioxide being primary products depending on the availability of surface oxygen, as was also described in Chapter 4.2.



On a fully oxidized surface, the oxygen transport by surface diffusion is expected to be fast. Carbon monoxide formed as in E15 would rapidly be further oxidized to carbon dioxide by reaction E16. When the surface becomes depleted of easily removable oxygen, the surface will be supplied with oxygen more and more by bulk diffusion from the cerium oxide phase. As the sample is reduced, the oxygen supply to the active sites is expected to become slower. Slow oxygen transport to the surface explains the decreasing conversion of methane and the increasing syngas selectivity with increasing degree of reduction in the cerium oxide.

After reduction in methane as the one presented in Figure 4.8, the material samples were regenerated. Both oxygen and carbon dioxide were tested as oxidants. Reoxidation of the cerium oxide and carbon removal could to a certain degree be obtained with carbon dioxide at high temperatures. However, it was found that oxygen was superior to carbon dioxide both for cerium oxide reoxidation (E18) and for carbon removal (E19-E20).





Complete regeneration of the material samples was obtained after treatment with pulses of oxygen. The experimental results gave no indications as to the role of platinum in equations E18-E21 although there is evidence in the literature that carbon dioxide can oxidize cerium oxide directly as in E21 [72]. Carbon gasification by carbon dioxide (E22) is endothermic and favored by high temperatures.

Figure 4.10a shows that during regeneration in pure oxygen, the cerium oxide reoxidation occurred simultaneously with the gasification of carbon deposits. Pure carbon monoxide comes off the sample until the material was completely regenerated. This shows that all the carbon deposits formed during reduction with methane could be selectively converted to carbon monoxide with oxygen.

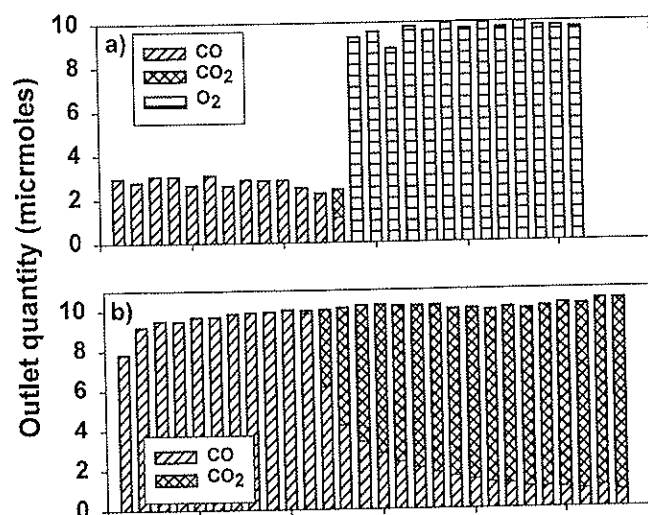


Figure 4.10: Regeneration of Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at 700 °C in pulses of a) oxygen and b) carbon dioxide after a treatment in methane as in Figure 4.8.

The high selectivity to carbon monoxide does not necessarily mean that the gasification itself is selective. It could also be a result of high activity between reduced cerium oxide and carbon dioxide. Carbon dioxide formed in the upper parts of the material bed through E20 could possibly readsorb and form carbon monoxide through E21. Regeneration of the reduced samples in carbon dioxide (Figure 4.10b) indeed showed oxygen uptake from carbon dioxide. It has also been reported in the literature that cerium oxide can take oxygen from carbon dioxide [72]. The high selectivity to carbon monoxide during the regeneration in oxygen is therefore likely to be a result of carbon dioxide reduction with reduced cerium oxide.

The study of the reaction between methane and promoted cerium oxide shows that synthesis gas indeed can be made with high selectivity and conversion at very low temperatures. Regeneration of the reduced solid material can easily be done with oxygen with simultaneous selective carbon gasification to carbon monoxide. The results show that a process where solid promoted cerium oxide is being treated in cycles with methane and gas phase oxygen can give far better yields than a steady-state partial oxidation of methane with gas phase oxygen at 700 °C.

These results are more thoroughly discussed in paper IV, which contains a description of the material preparation, the material characterization data and some pulse experiments with methane, oxygen and carbon dioxide in gas-solid reaction with promoted cerium oxide. This study indicated promising features of the material and the possibility to produce syngas at lower temperatures than what is usually applied in the production of synthesis gas. It was therefore desirable to study the gas-solid reaction not only in reactions with pulses of reactants but also under steady alternating flows of methane and oxygen in repeated cycles. This was done and some results are given in appendix V. It appears that full methane conversion can be achieved and high purity syngas can indeed be formed when promoted cerium oxide is treated in alternating feed cycles of methane and oxygen. The state of the solid material can be controlled by carefully regulating the time in which the material is exposed to methane and oxygen respectively.

Equilibrium calculations valid for steady-flow conversion of methane and oxygen (feed ratio 2:1) shows that full methane conversion is not thermodynamically

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obtainable at 700 °C [25]. Cyclic operation of this gas-solid reaction system therefore enables the conversion to be pushed beyond equilibrium for steady-state operation.

## 5 Conclusions

Hydrogen and carbon monoxide can indeed be formed from the catalytic direct partial oxidation of methane without going through reforming processes. This has been shown experimentally with a Pt/Rh gauze catalyst at short contact time conditions with incomplete reactant conversions at high temperatures. However, the experimental data also shows that the yield of syngas through such a direct route is limited because the products are more reactive for combustion than the reactant methane.

The reactivity of adsorbed oxygen species towards oxidation of the various synthesis gas components was further studied in detail. It was found necessary to attempt to constrain the supply of oxygen to the active sites in order to suppress combustion processes. It was found that at the conditions used for the partial oxidation of methane, platinum does not only adsorb oxygen on the surface, but oxygen is also absorbed into the bulk of the metal. This implies that the active sites on the surface can be supplied with oxygen not only by gas phase adsorption, but also by solid diffusion from the metal bulk. The latter being very slow compared with the former. It was found that the selectivity to carbon monoxide and hydrogen increased drastically in absence of gas phase oxygen, when oxygen was supplied to the active sites uniquely by solid diffusion.

The partial oxidation of methane in absence of gas phase oxygen was further studied using Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> as an intermediate solid oxygen reservoir. This material was treated in cycles of methane and oxygen. The γ-Al<sub>2</sub>O<sub>3</sub> provided high surface area and thereby good contact between the reactant gases and the solid material. The cerium oxide provided a suitable dynamic oxygen reservoir and the presence of platinum gave high activity for the conversion of methane. The results showed that synthesis gas could be formed with high selectivity and at full conversion of methane from the gas-solid reaction at as low temperatures as 700 °C. The solid material was easily regenerated with oxygen.

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obtainable at 700 °C [25]. Cyclic operation of this gas-solid reaction system therefore enables the conversion to be pushed beyond equilibrium for steady-state operation.



monoxide) can easily be applied in a syngas stream. However, if the regeneration is performed with air, the effluent will be a mixture of carbon monoxide and nitrogen. Such an effluent can only serve as fuel and will cause a reduction in the process carbon efficiency. The possible economic advantage of eliminating the need for an oxygen plant is therefore accompanied by an economic disadvantage caused by reduced carbon efficiency. The possibility of eliminating the need of an oxygen plant is still very interesting and can be of major importance and benefit in certain applications. This holds particularly in favor of small-scale facilities where oxygen plants would be out of the question. Carbon formation should therefore be studied and minimized in order to reduce the negative economic impact on the carbon efficiency. If carbon formation is avoided, this could open the possibility for such a reactor system to work efficiently both as an air separator and as a syngas generator.

There is also still room for improving the dynamic performance of the solid Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. There are indications in the literature [60] that improving the oxygen transport rate in the solid phase by using mixed ceria and zirconia can lead to lower syngas selectivity. It is therefore the author's opinion that the material components separately each fulfill adequately their functions. The surface area of the γ-Al<sub>2</sub>O<sub>3</sub> support used in this study was not of the highest. A support with higher surface area can significantly increase the material performance. The weight loading of cerium oxide can probably be further optimized. The weight loading and dispersion of the platinum is also evidently of large importance for the cost-efficiency of the material. As high dispersion as possible of the platinum is desirable. Different procedures for adding the platinum to the CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> should be studied.

It is also the author's opinion that even though optimization of all these parameters will give significant improvements, the GHSV will never by far approach what is obtained in commercially available ATR reactors. It is the author's opinion that ATR technology will dominate large-scale syngas production even more in the future. Marginal improvements based on fundamental technological changes are rarely taken to application by the industry. The gas-solid reaction system could therefore possibly be attractive in other applications than large-scale natural gas conversion facilities.

The main advantages of the gas-solid reaction system is:

- It gives an opportunity of eliminating an oxygen plant. This is maybe the advantage with highest economic potential.
- The cyclic gas-solid process can be operated at significantly lower temperatures than conventional syngas processes.
- The possibility to produce syngas with complete conversion of methane is very beneficial both for the process carbon efficiency and for avoiding inert methane in a downstream recycle process.
- The economy of scale is not as evident for this cyclic gas-solid reaction system as it is for ATRs that need to operate with extremely high gas velocities.

This all point towards a possible application in small-scale synthesis gas production units. Conventional synthesis gas production is strongly influenced by economy of scale. There has therefore been a large threshold for making production units. The demand for syngas has had to be very large before it is considered economically feasible to produce it. However, in the future, it is likely to believe that more demand for smaller volumes of hydrogen/syngas will arise. Small fuel cell electrical power generators will need small-scale hydrogen production equipment. Petroleum refineries could also need small hydrogen production units. It is therefore the author's opinion that if a process based on a cyclic gas-solid reaction system should be developed, it should be aimed towards a totally different market than what conventional ATR and tubular reforming units are intended for.

Finally, it must be emphasized that the work with the cyclic gas-solid reaction system, in this particular study, has been motivated by providing the necessary chemistry behind a possible new way of making synthesis gas. Optimization of the material performance has so far not been the main aim of the work. Systematic engineering with the above mentioned parameters should be done in order to determine the optimal efficiency of a process. A final judgement to whether or not such a process is economically advantageous must be based upon an optimally performing material.

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## List of appendices

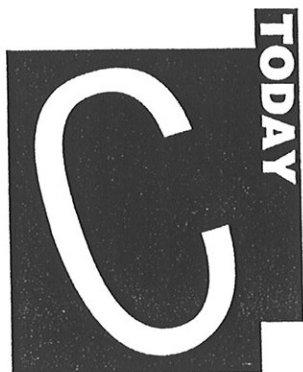
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- II M. Fathi, O.A. Rokstad and A. Holmen, "Partial oxidation and steam reforming of methane over platinum/rhodium metal gauze catalysts at very short contact times", *Manuscript accepted for publication in Catalysis Letters*.
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+ **Errata**
- IV M. Fathi, E. Bjørgum, T. Viig and O.A. Rokstad, "Partial oxidation of methane: Elimination of gas phase oxygen", *in press, Catalysis Today*
- V J.C. Jalibert, M. Fathi, O.A. Rokstad and A. Holmen, "Synthesis gas production from methane with promoted cerium oxide by a cyclic gas-solid reaction", *Abstract accepted for presentation at the 6<sup>th</sup> Natural Gas Conversion Symposium, Alaska USA, June 2001*.







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Partial oxidation of methane to synthesis gas  
at very short contact times

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## Partial oxidation of methane to synthesis gas at very short contact times

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### Abstract

Catalytic partial oxidation of methane has been studied over Pt, Pt/Rh, Pt/Ir and Pd gauze catalysts at contact times in the range 0.00021–0.00033 s. The experiments were carried out at 1 bar and 700–1100°C using a single gauze in a quartz reactor heated in an electric furnace. The feed consisted of CH<sub>4</sub>, O<sub>2</sub> and inert (Ar) and with different ratios between CH<sub>4</sub> and O<sub>2</sub>. High selectivities to CO were observed at high temperatures. However, the selectivity to H<sub>2</sub> was always rather low (below 30% in most cases) at these conditions with incomplete conversion of O<sub>2</sub>. Alloying the Pt gauze with Rh improves the selectivity to synthesis gas as well as the time on stream behaviour. The effect of the CH<sub>4</sub>/O<sub>2</sub> ratio depends on the gauze. The selectivity to synthesis gas decreased with increasing amount of O<sub>2</sub> on the Pt gauze whereas the opposite effect was observed on a Pt/Rh gauze. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Synthesis gas; Methane; Gauze catalysts; Partial oxidation

### 1. Introduction

Two different routes exist for the conversion of methane to fuels and chemicals, either via synthesis gas or directly to C<sub>2</sub> hydrocarbons or methanol. Commercial processes for methane conversion are all based on synthesis gas. Steam reforming is the dominant process for production of synthesis gas [1]. However, oxidation reactions are generally much faster than steam reforming suggesting that synthesis gas could be produced in smaller reactors by using O<sub>2</sub> instead of steam.

It is usually observed that the catalytic partial oxidation of methane consists of two steps: Total oxidation of part of the methane followed by H<sub>2</sub>O and CO<sub>2</sub> reforming [2]. However, different proposals exist regarding the formation of primary products in the catalytic partial oxidation of methane [3–6]. A large research effort is presently being carried out on the catalytic partial oxidation of methane to synthesis gas [7].

Since the reforming reactions are slower than the oxidation reactions it should be possible to study the partial oxidation without being influenced to any large extent by secondary reactions at very short contact times. In fact, by using gauze catalysts it has been shown that the partial oxidation can be studied at such conditions [3,8]. High temperature reactions at extremely short contact times are also interesting in many

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other applications [9]. The present work was initiated in order to study the behaviour of different gauzes on the partial oxidation of methane.

## 2. Experimental

The following metal gauzes (supplied by K.A. Rasmussen) were used: Pt, Pt/5%Rh, Pt/10%Rh, Pt/10%Ir and Pd. The gauzes were woven from metal wires with different diameters. The Pt/10%Rh and the Pt/5%Rh gauzes were woven into 1024 meshes/cm<sup>2</sup> from wires with a diameter of 60  $\mu$ m and the Pt gauze (256 meshes/cm<sup>2</sup>) was made from a 90  $\mu$ m wire. Experiments have also been carried out with a Pt gauze of the same size as the Pt/Rh gauzes (Fig. 1(a) and (b)). The Pt/10%Ir and the Pd gauzes had 250 meshes/cm<sup>2</sup> (120  $\mu$ m wire) and 256 meshes/cm<sup>2</sup> (180  $\mu$ m wire), respectively. Before use the Pt/10%Rh gauze has a surface area of 0.005 m<sup>2</sup>/g [10]. Since the different gauzes had different mesh sizes (and wire diameters) it means that the reactor volume and the space times are not exactly the same at a constant feed rate.

The experiments were carried out in a conventional flow apparatus using a quartz reactor with a circular

gauze held between two cylindrical pieces of a ceramic monolith (Cordierite from Corning, 400 cells/in.<sup>2</sup>). The diameter of the gauze, the monolith pieces and the reactor was 15 mm. The quartz reactor was placed inside a furnace. The gauze temperature was measured by a moveable thermocouple inside the reactor, and controlled by careful regulation of the furnace temperature. In addition to the moveable thermocouple, an optical pyrometer was also used to measure the gauze temperature. The two methods gave almost identical values.

The products were analysed by gas chromatography. Prereduction of the gauze was carried out in situ with H<sub>2</sub> at 600°C for 1½ h. The gauze was then heated to 920°C in argon atmosphere. The methane and oxygen diluted in argon were introduced, and the ignition caused the gauze temperature to rise to above 1000°C. The gauze was then cooled to the desired temperature by temporarily turning off the heat and venting the furnace if necessary.

## 3. Results and discussion

Experiments were initially performed without any catalyst present and also without the two pieces of

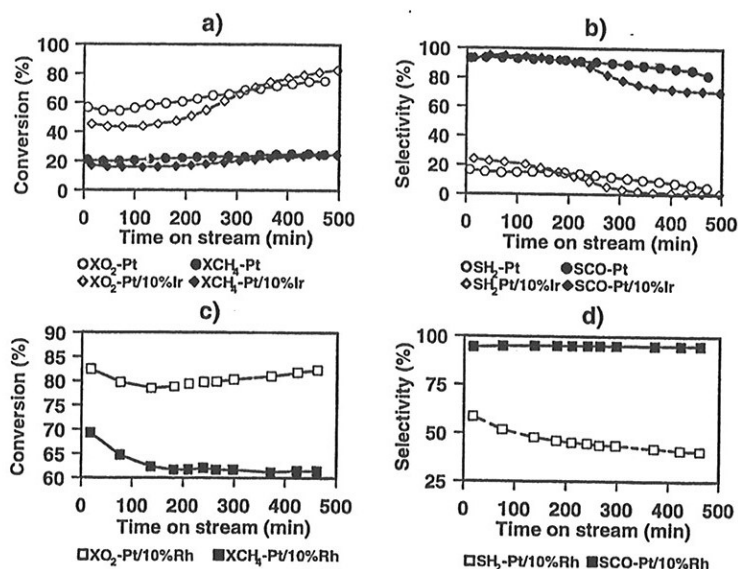


Fig. 1. Effect of time on stream: (a), (b) Conversion ( $X$ ) and selectivity ( $S$ ) over Pt (1024 meshes/cm<sup>2</sup>) and Pt/10%Ir gauzes at 990°C and CH<sub>4</sub>:O<sub>2</sub>:Ar feed ratio of 2:1:10. (c), (d) Conversion and selectivity over a Pt/10%Rh gauze at 1100°C and CH<sub>4</sub>:O<sub>2</sub>:Ar feed ratio of 2:1.6:9.4. The total gas flow is 2000 N ml/min.

cordierite in the reactor but at exactly the same conditions as with a gauze present. Initiation of the methane oxidation without any catalyst requires very high temperatures. The conversion of methane was less than 5% at 1000°C. Small amounts of C<sub>2</sub> were observed with a maximum selectivity to C<sub>2</sub>H<sub>6</sub> of 50% at 850°C. CO<sub>2</sub> was the main carbon oxide below 970°C. The cordierite did not influence the conversion of CH<sub>4</sub>, but the C<sub>2</sub>-formation was higher with the pieces of cordierite in the reactor (maximum selectivity of 75%).

The activity, selectivity and stability of the different gauzes were studied as a function of the temperature and the ratio between CH<sub>4</sub> and O<sub>2</sub> in the feed. The gauzes show different ignition temperatures at a total feed rate of 2000 Nml/min and a feed composition of CH<sub>4</sub>:O<sub>2</sub>:Ar=2:1:10. The following ignition temperatures were observed: Pt: 800°C, Pt/5%Rh and Pt/10%Ir: 820°C, Pt/10%Rh: 880°C and Pd: 620°C. However, due to the formation of PdO the Pd gauze was not suitable for studying the partial oxidation of methane at high temperature.

The time on stream behaviour of the different gauzes is shown in Fig. 1(a)–(d). The Pt and the Pt/10%Ir gauzes loose syngas selectivity as time on stream increases (Fig. 1(a) and (b)). It was observed that the temperature in the monolith downstream of the gauze increased during an experiment indicating that metal is possibly transported from the gauze to the monolith where it causes secondary combustion of both CO and H<sub>2</sub>.

The Pt/10%Rh gauze has been studied at different conditions, e.g. higher temperatures. It is of interest to recognize that a much higher conversion of methane is obtained with the Pt/10%Rh gauze compared with the Pt (and the Pt/10%Ir) gauze, but the conversion of oxygen is about the same after 500 min on stream. A major difference is also observed in the selectivity of hydrogen. However, it must be emphasized that the results for the Pt gauze given in Fig. 1 are obtained at 990°C whereas 1100°C (and a different feed composition) was used for the Pt/10%Rh gauze. The Pt and the Pt–Rh gauzes in Fig. 1 have the same mesh size (1024 meshes/cm<sup>2</sup>). No temperature increase was observed downstream of the Pt/10%Rh gauze and it is believed that the decrease in the selectivity of H<sub>2</sub> is caused by a change in the surface properties of the metal rather than metal migration. It is well known

from ammonia oxidation that alloying the Pt gauze with Rh increases the stability of the gauze [11].

The conversion and the selectivity of the Pt and Pt/Rh gauzes have been studied at different temperatures and CH<sub>4</sub>:O<sub>2</sub> ratios in the feed. The experiments at different temperatures have been carried out in the following way: The gauze was cooled down rapidly after ignition and the temperature was then increased in steps of 100°C to 1100°C, and thereafter reduced in the same way to 700°C. Analysis of the product gas was performed at each temperature level and the results are shown in Fig. 2(a)–(d). The high temperatures were not held for long periods of time and no significant ageing of the catalyst was observed.

Fig. 2 clearly shows that the increase in conversion of methane and oxygen with temperature is very low indicating that the reaction rate is controlled by mass transfer limitations. For the Pt gauze the conversion is almost constant and independent of the temperature. At higher temperatures the linear gas velocity will increase and the space time decrease due to the fact that the experiments have been performed at a constant feed rate. The increased gas velocity means that at higher temperatures larger parts of the reactants may pass through the gauze without having any contact with the metal. The Pt gauze in Fig. 2 has a much more open structure than the Pt/Rh gauzes (256 and 1024 meshes/cm<sup>2</sup>, respectively). This will give a less distinct temperature response for the Pt gauze compared with the Pt/Rh gauzes.

As expected the selectivity to syngas increases with increasing temperature and at 1000°C the selectivity to CO is more than 95% for the Pt/10%Rh gauze. At these conditions with incomplete conversion of O<sub>2</sub> the selectivity to H<sub>2</sub> is rather low and in addition there is a large difference between the Pt and the Pt/Rh gauzes. It has been reported that Rh-impregnated monoliths are superior to Pt monoliths for the production of syngas, an observation which has been explained by the higher heat of adsorption of oxygen on Rh than Pt [12].

The ratio of CH<sub>4</sub> to O<sub>2</sub> in the feed has been varied from 1.3 to 4 and the results at 900°C for the Pt and Pt/5%Rh gauzes are given in Fig. 3. The results clearly show that for the Pt gauze the conversion of methane decreases and the selectivity to syngas increases with increasing CH<sub>4</sub>:O<sub>2</sub> ratio in the feed. However, for the

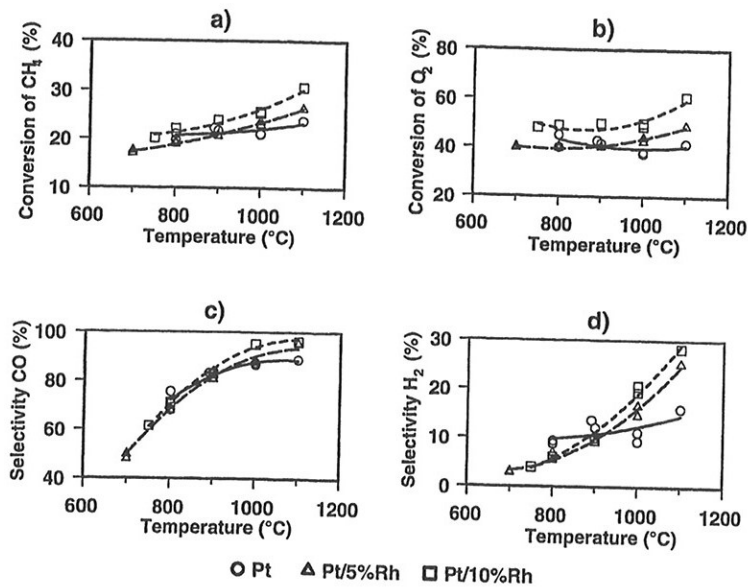


Fig. 2. Influence of gauze temperature on conversion and selectivity over Pt (256 meshes/cm<sup>2</sup>) and Pt/Rh gauzes. Total gas flow is 2000 Nml/min and the CH<sub>4</sub>:O<sub>2</sub>:Ar ratio is 2:1:10.

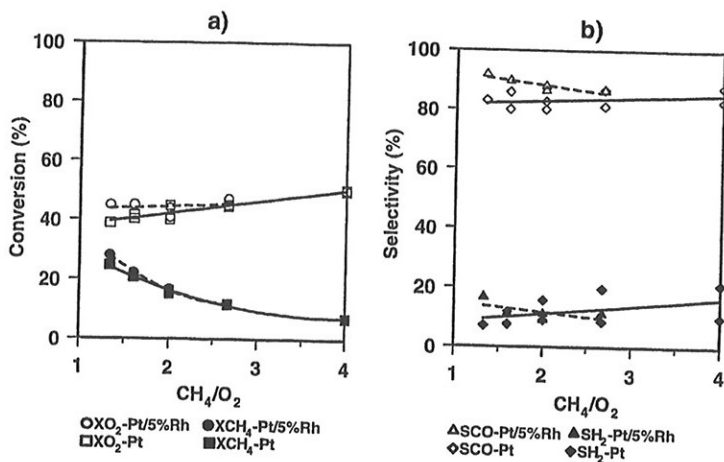


Fig. 3. Conversion (X) and selectivity (S) over a Pt and a Pt/5%Rh gauze as function of CH<sub>4</sub>/O<sub>2</sub> ratio in the feed gas, T=900°C, total gas flow=2000 Nml/min.

Pt/5%Rh gauze the selectivity to syngas decreases with increasing CH<sub>4</sub>:O<sub>2</sub> ratio indicating that the higher partial pressure of O<sub>2</sub> changes the oxidation state of the surface or/and the surface composition.

The results presented in Fig. 1(c) and (d) are obtained using a CH<sub>4</sub>:O<sub>2</sub> ratio of 2:1.6 in the feed. It has been shown that the steady-state conversion of methane on the Pt/10%Rh gauze at 1100°C increases



from 30% with  $\text{CH}_4:\text{O}_2=2:1$  to 60% using  $\text{CH}_4:\text{O}_2=2:1.6$ .

#### 4. Conclusion

The Pt/Rh gauzes are superior to the Pt gauze as far as syngas selectivity and time on stream stability are concerned. For the Pt/5%Rh gauze the selectivity to  $\text{CO}+\text{H}_2$  increases with increasing concentration of  $\text{O}_2$  in the feed whereas the opposite effect is observed for the Pt gauze. Noble metal gauzes are very effective for combustion of  $\text{H}_2$ .

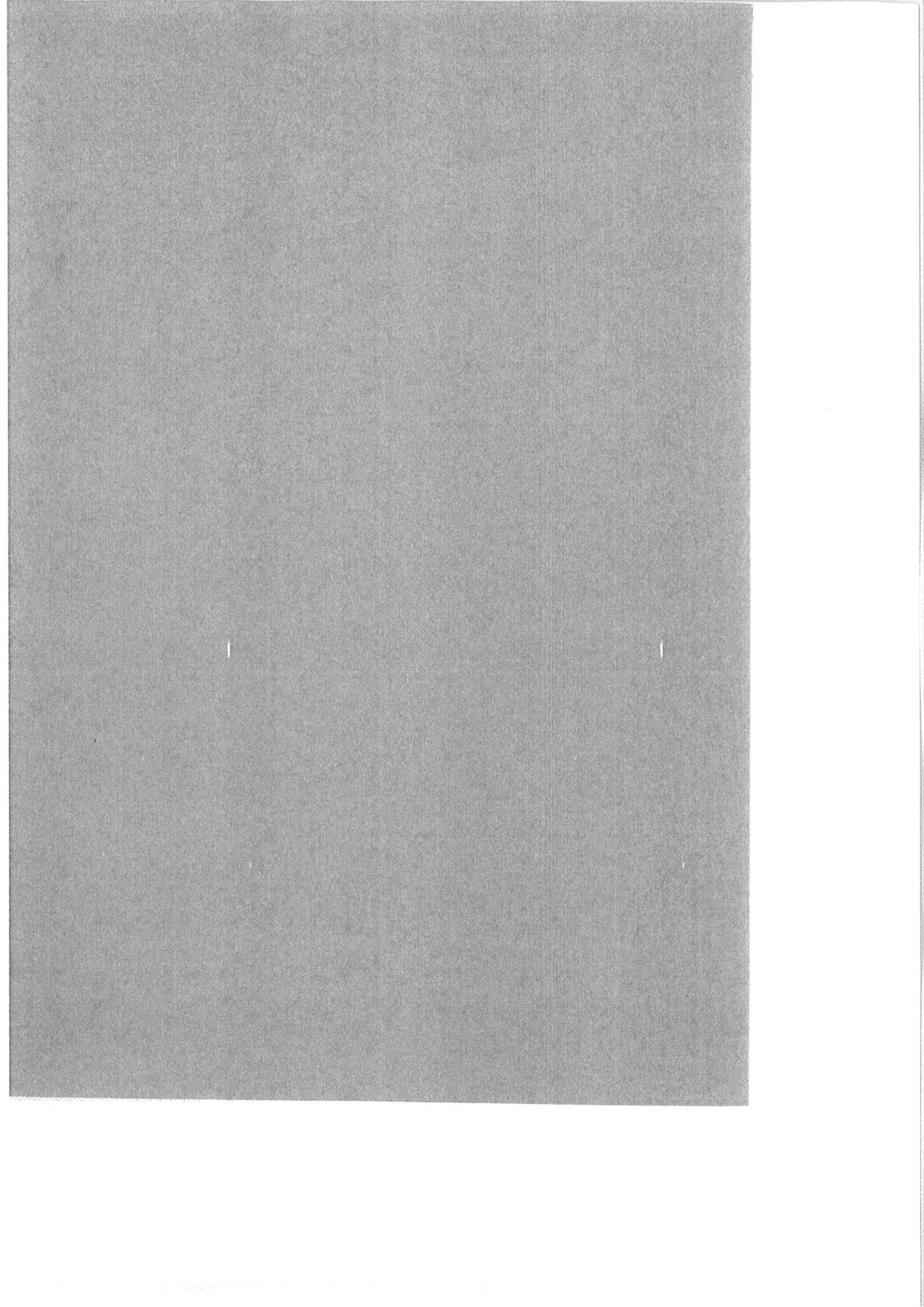
#### Acknowledgements

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# Partial oxidation and steam reforming of methane over platinum/rhodium metal gauze catalysts at very short contact times

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**Keywords:** Methane partial oxidation, steam reforming, synthesis gas, noble metal gauzes, short contact times.

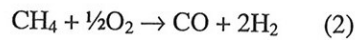
## Abstract

The extent of reforming reactions during partial oxidation of methane over Pt/Rh gauzes has been studied in a conventional flow apparatus. The experiments have been performed at extremely low contact times, 1 bar pressure, high temperatures (1000-1050 °C) and with various feed compositions such as CH<sub>4</sub>:H<sub>2</sub>O:Ar = 2:1:10 and CH<sub>4</sub>:O<sub>2</sub>:H<sub>2</sub>O:Ar = 2:1:1:9 at 1050 °C. No significant extent of reforming reactions was observed at a contact time of 0.21 ms. Experiments have also been conducted using a feed ratio of CH<sub>4</sub>:O<sub>2</sub>:Ar = 2:1:4 over a large range of contact times at 1000 °C. The results show that the selectivity to H<sub>2</sub> strongly depends on the contact time. At low flow rates resulting in a complete conversion of O<sub>2</sub>, H<sub>2</sub> can be produced with high selectivity. At the highest flow rates studied, with incomplete O<sub>2</sub> conversion, the selectivity to H<sub>2</sub> increases with decreasing contact time. In between these two extremes there is an area with very low H<sub>2</sub> selectivity due to the conversion of H<sub>2</sub> with

O<sub>2</sub>.

### Introduction

Synthesis gas can be produced by steam reforming (1), by partial oxidation (2) or by combinations of these two reactions [1]:



It is usually observed that the partial oxidation of methane consists of two steps: Initial combustion of part of the methane followed by H<sub>2</sub>O and CO<sub>2</sub> reforming and the water-gas shift reaction [2-4]. This is also the principle behind the autothermal reformer (ATR) which consists of a combustion section with a special burner and a catalytic section where the equilibrium composition is approached [1]. The equilibrium composition of the product gas is determined by the temperature at the reactor exit. The temperature in the combustion section is very high, but the temperature decreases rapidly through the catalytic section due to the endothermic reforming reactions. High selectivities of CO and H<sub>2</sub> require high temperatures and it is therefore desired to operate at a high exit temperature. The exit temperature is set by the adiabatic heat balance and it is limited by the maximum tolerable temperature in the combustion section. High yields of H<sub>2</sub> are most strongly depending on high temperatures.

To avoid the high temperatures needed to make synthesis gas by the autothermal route, research has recently been directed towards the direct production of CO and H<sub>2</sub> without going through combustion and subsequent reforming. It has been suggested

that this could imply the possibility of producing synthesis gas with better selectivity than predicted by thermodynamic equilibrium [4]. It should be noted, however, that comparisons between experimental results and equilibrium calculations are difficult due to the problems of measuring real temperatures [5]. It has been shown that in some systems under certain conditions, CO and H<sub>2</sub> can be regarded as primary products of the reaction [6-16]. By avoiding further oxidation of CO and H<sub>2</sub> synthesis gas could then be produced at moderate temperatures. Reforming reactions are generally slower than oxidation reactions and the direct formation of CO and H<sub>2</sub> should therefore be observed in reactor systems with extremely short contact times and low reactant conversions. This can be obtained with high gas flow rates over noble metal gauzes [6,7, 12- 16]. The direct formation of CO and H<sub>2</sub> is also observed over some catalysts under vacuum conditions in TAP-reactors [8].

In this context it should also be mentioned that some studies conclude with that carbon dioxide can be primary product of the methane oxidation over Rh [17]. This particular study was conducted on 1 wt%Rh/γ-Al<sub>2</sub>O<sub>3</sub> and concluded that the nature of the primary products from rhodium catalyzed partial oxidation of methane depended on the surface reduction of the rhodium. In cases with a catalyst with low metal loading on a high support surface area, oxygen spillover from the support can be significant [8]. Spillover of oxygen from the support can give better oxygen availability on the active metal sites and therefore lead to different results from studies conducted over pure metals without the influence of a support.

One of the objectives of this study was to determine the extent of the reforming reactions during catalytic partial oxidation of methane at extremely short contact times

using metal gauzes made of Pt/Rh. These gauzes have previously been used for studying the catalytic partial oxidation of methane [6, 7, 9, 12, 15] and the oxidative dehydrogenation of C<sub>2</sub>-C<sub>3</sub> hydrocarbons [16, 18]. For short contact time oxidative conversion of C<sub>2</sub> and higher hydrocarbons it seems that noble metal catalysts provide extremely rapid heating of the reactants due to the increased importance of combustion. The oxidative dehydrogenation has been shown to mainly take place in the gas phase [18, 19]. Because of the high temperatures applied, the rate limiting step in these systems is well accepted to be mass transport of oxygen to the catalytic surface [9, 15, 20].

### **Experimental**

The experiments were carried out in a conventional flow apparatus using a quartz reactor with a circular gauze held between two pieces of a ceramic monolith (Cordierite from Corning, 400 cells/in<sup>2</sup>). The metal gauzes applied were Pt/5%Rh and Pt/10%Rh alloys, woven to 1024 meshes/cm<sup>2</sup> from a wire with a diameter of 60 μm. A schematic drawing of the reactor is shown in Figure 1. The diameter of the cylindrical reactor as well as of the gauze and the monoliths is 15 mm and the reactor is placed inside an electrical furnace. A moveable thermocouple (chromel-alumel protected by a quartz tube) placed in the center of the reactor allowed measurement of the gauze temperature. The temperature at the gauze was regulated through the temperature in the electrical furnace. Reactors with gauze catalysts and high flow rates are well described in the literature [6, 16, 20]. All temperatures referred to below are the temperatures measured by the moveable thermocouple. It has been shown previously [6, 7, 9] that this temperature measurement represents the gauze temperature more than the gas temperature. The experiments were carried out with

one to four layers of Pt/Rh gauzes held in the reactor at the same time. The metal gauzes were reduced in  $H_2$  for 1½ hours at 600 °C. The temperature was raised to 920 °C in Ar and the reactant gases, consisting of  $CH_4$  and  $O_2$  diluted in Ar, were fed to the gauze reactor. The heated reactor volume downstream of the gauze was minimized and the products were analyzed by gas chromatography as described previously [7]. The contact time was calculated from the free volume of the gauze and the gas flow rate at normal conditions (atmospheric pressure and 0 °C).

Figure 1

### Results and discussion

Production of  $H_2$  can be obtained by direct partial oxidation of methane at certain conditions. The selectivity to  $H_2$  depends strongly on parameters such as temperature, feed composition, catalyst and contact time [9, 20]. In order to study the possible contribution to  $H_2$  formation by steam reforming, experiments were conducted with  $H_2O$  replacing  $O_2$  at very short contact times. No reaction occurred ( $X_{CH_4} < 1\%$ ) over a single layer of Pt/10%Rh gauze catalyst at 1050 °C and  $\tau=0.21$  ms using a feed consisting of  $CH_4:H_2O:Ar = 1:1:10$ . However, at a steam/carbon ratio of 1.0, carbon formation may occur and this could inhibit catalytic reactions on the metal surface.

Experiments have also been carried out in the presence of both  $H_2O$  and  $O_2$  by switching the feed composition from  $CH_4:O_2:Ar = 2:1:10$  to  $CH_4:O_2:H_2O:Ar = 2:1:1:9$  at 1050 °C and  $\tau=0.21$  ms. At these conditions carbon formation was less likely to take place. No significant difference in the conversion or selectivity was observed as shown in Figure 2. Steam reforming would result in an increase in the selectivity to



both CO and H<sub>2</sub>. However, the water-gas shift reaction (3) could also take place.



According to this reaction, the presence of water would result in a decrease in the CO selectivity and an increase in the H<sub>2</sub> selectivity. Since the CO selectivity can be affected in opposite directions by steam reforming and water-gas shift, the constant CO selectivity alone is not enough information to conclude. However, both steam reforming and water-gas shift are expected to increase the H<sub>2</sub> selectivity. As shown in Figure 2, the selectivity to H<sub>2</sub> also seemed to be unaffected by the presence of water. It is therefore likely that neither steam reforming nor water-gas shift took place to any large extent at these conditions of very short contact times.

Figure 2

If the contact time was too short for total combustion and reforming to take place, a longer contact time should allow the conversion of oxygen to be complete and finally result in an increase in the selectivity to synthesis gas from H<sub>2</sub>O and CO<sub>2</sub> reforming. In other words, the product gas mixture should approach the equilibrium composition. Another set of experiments was therefore carried out at 1000 °C by using up to four Pt/5%Rh gauzes and with feed flow rates varying from 2000 Nml/min to 300 Nml/min. The feed composition was kept constant with a CH<sub>4</sub>:O<sub>2</sub>:Ar ratio of 2:1:4 as in a natural gas/air mixture. The furnace temperature outside the reactor had to be raised at higher contact times to maintain the gauze temperature at 1000 °C. At  $\tau=0.21$  ms and  $\tau=5.4$  ms, the furnace temperatures were 825 and 971 °C, respectively. The

results are shown in Figure 3.

Figure 3

About 50% conversion of  $O_2$  was obtained at a contact time of 0.21 ms and the conversion of  $O_2$  was complete at  $\tau=3.2$  ms. The conversion of methane was only slightly increased with increasing contact time at the conditions studied. Of particular interest is the selectivity to  $H_2$ . The selectivity to  $H_2$  increased with decreasing contact time at the shortest contact times included in this study. The  $H_2$  selectivity passed through a broad minimum and increased again at longer contact times. At conditions with complete conversion of  $O_2$ , the production of  $H_2$  by steam reforming started to be important and the selectivity increased rapidly with increasing contact time. These results lead to the conclusion that on the Pt gauzes  $H_2$  reacts with  $O_2$  resulting in very low selectivity to  $H_2$  except at the shortest contact times studied. At contact times below 1.5 ms the selectivity of  $H_2$  was found to increase with decreasing contact times.

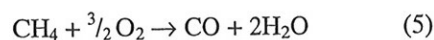
However, gas phase reactions should also be considered although previous experiments have shown very low conversion of  $CH_4$  at 1000 °C and similar conditions using  $O_2$  in an empty reactor [9]. The moveable thermocouple can give a good measurement of the gauze temperature since this is the main source of heat radiation inside the reactor. However, the moveable thermocouple does by no means allow measurements of the actual gas temperature throughout the reactor. The pieces of cordierite monolith provided fairly good radiation shielding from the furnace and the gauze. It is therefore still believed that a reasonably good qualitative image of the

trend in the temperature profile can be deduced from measurements with the thermocouple also when positioned away from the gauze. Comparisons between experiments can reveal qualitative differences. As shown in figure 4 the measured temperature profile through the reactor depended on the feed flow rate. As already mentioned it was desirable to maintain the same gauze temperature of 1000 °C throughout the whole range of contact times. In order to accomplish this, the temperature in the furnace surrounding the reactor had to be varied over an interval of about 150 °C. This temperature was lowest (825 °C) with the highest flow rate and was increased towards 971 °C as the gas flow rate was decreased. Since the combustion of hydrogen with oxygen can proceed both in the gas phase and on the catalyst surface, the increased content of H<sub>2</sub> in the product gas at extremely low contact times could also be a result of a lower temperature downstream of the gauze. The low temperature downstream of the gauze is caused by the lower furnace temperature and thereby also a lower actual temperature in the feed gas to the gauze. This also gives a lower temperature in the fraction of the feed gas that bypasses the catalyst wires and quenches the product gas. There will also be a higher heat loss from the reactor when the temperature in the furnace surrounding it is lower. A higher gas temperature, as in the case with higher contact times, would therefore also give a higher contribution from gas phase reactions and thereby also a lower selectivity to H<sub>2</sub>.

In summary, the results from figures 2 and 3 are a very strong indication that H<sub>2</sub> is formed directly from CH<sub>4</sub> at very short contact times. Gas phase reactions are more likely to occur with H<sub>2</sub> than with CH<sub>4</sub>. Higher contact times and more external heating can therefore also lead to more gas phase combustion and thereby a lower H<sub>2</sub>

selectivity.

The results shown in Figure 3 clearly demonstrate that the selectivity to CO was high throughout the whole range of contact times studied. It was in fact highest at conditions with incomplete O<sub>2</sub> conversion. Previous results using higher dilution [7] have also shown that the CO selectivity increases with decreasing contact time. The total combustion to CO<sub>2</sub> does not take place to any large extent. The point of minimum H<sub>2</sub> selectivity is best described through the partial combustion reaction (5) which is the sum of partial oxidation of CH<sub>4</sub> (2) and the combustion of H<sub>2</sub> on the surface of the gauze or in the gas phase (4):



However, the selectivity to carbon dioxide was never less than about 15% at 1000 °C. Water gas shift (3) was found not to take place at extremely short contact times above. It therefore seems that carbon dioxide to a certain degree can be formed directly from CH<sub>4</sub> but with considerably lower selectivity than for CO. It is well established that mass transport of O<sub>2</sub> to the surface is rate limiting at these conditions [9, 15, 20]. This means that the concentration of adsorbed oxygen on the surface is low. This is supported by the low selectivity to H<sub>2</sub> that is caused by the high reactivity between hydrogen and oxygen. High selectivity to CO at the shortest contact times is therefore likely to result from a low coverage of oxygen. It could seem that hydrogen in a way keeps the surface clean of oxygen. A study reported in the literature shows how isotopic labeling of molecules can reveal the mechanism of formation of CO at higher

contact times [10]. The high selectivity to  $H_2$  at contact times above 4 ms shows that at higher contact times also reforming reactions can take place and thereby give multiple pathways to the formation of CO. Therefore these results do not give enough information to make conclusions about the main pathways in the formation of CO except at extremely short contact times.

At contact times above 3.0 ms the selectivity to  $C_2$  also becomes significant indicating that  $CH_x$  species desorb from the noble metal surface and recombine in the gas phase close to the gauze before being oxidized to carbon oxides. This was also confirmed from the temperature profiles shown in Figure 4. At very high contact times (low flow rates) the temperature maximum in the reactor was in fact upstream of the catalyst gauze showing that gas phase reactions with  $CH_4$  indeed must take place.

The contact time was manipulated through varying the gas flow rate through the reactor. The flow rate was varied over a large range from 300 Nml/min to 2000 Nml/min. At these conditions the conversions of  $CH_4$  were 45% and 22% respectively. In an absolute term such as the overall reaction rate (moles of  $CH_4$  reacted per second) the trend is opposite than the trend of conversion (which is a relative term). The overall reaction rate increases with decreasing contact time both for methane and for oxygen. Approximately three times more  $CH_4$  (moles/sec) was turned over with a total feed flow rate of 2000 Nml/min and a conversion of 22% than in the case with 300 Nml/min and a conversion of 45%. In addition, the contact time was more than one order of magnitude shorter (0.2 ms compared to 5.4 ms). For oxygen the overall reaction rate was twice as high at 0.2 ms than at 3.2 ms where the conversion became complete and leveled out. This shows that the overall catalyst

effectiveness benefits from high linear gas velocities. This is in perfect agreement with that mass transport is rate determining. Increased gas velocity reduces the film thickness and thereby increases the overall catalyst effectiveness factor.

Extrapolating the curves in Figure 3 towards even shorter contact times indicates that the  $H_2$  selectivity could be even higher. However, the fact that both  $CH_4$  and in particular the  $O_2$  conversion would be lower is evident. These results therefore lead to the conclusion that the design of an efficient catalyst for the direct partial oxidation of methane is impossible unless the activity for the combustion of  $H_2$ , reaction (4), is very low. At high temperatures reaction (4) is likely to occur in gas phase as well as on the catalyst surface. This means that the catalyst in addition must be able to work at low temperatures where no gas phase reactions occur.

### Conclusions

- Mass transport limitations are very important for the effectiveness of the Pt/Rh gauze catalysts when working at temperatures around 1000 °C.
- The results clearly indicate that the partial oxidation of  $CH_4$  can be studied at very short contact times without being influenced by steam reforming or water-gas shift.
- The potential yield of  $H_2$  produced in this way over noble metal gauzes is however limited because of secondary combustion with  $O_2$ . Hydrogen is more reactive than the unconverted reactant  $CH_4$  in the reaction with  $O_2$ .
- Equilibrium composition can be reached at higher contact times by steam reforming and the water-gas shift reaction.

### Acknowledgements

The financial support from the Norwegian Research Council is greatly acknowledged.

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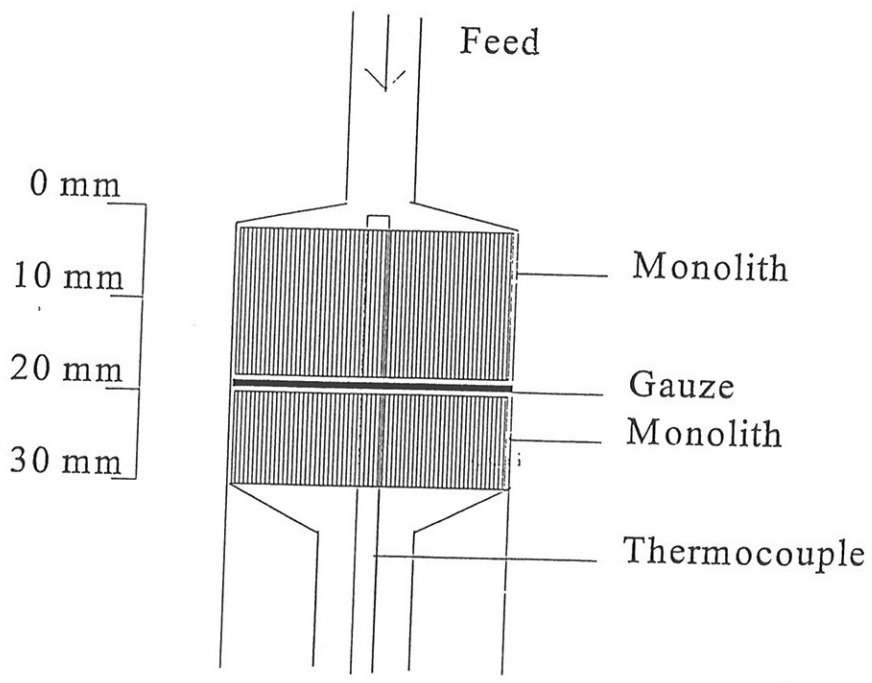


Figure 1: Reactor for noble metal gauze catalysts at millisecond contact times.

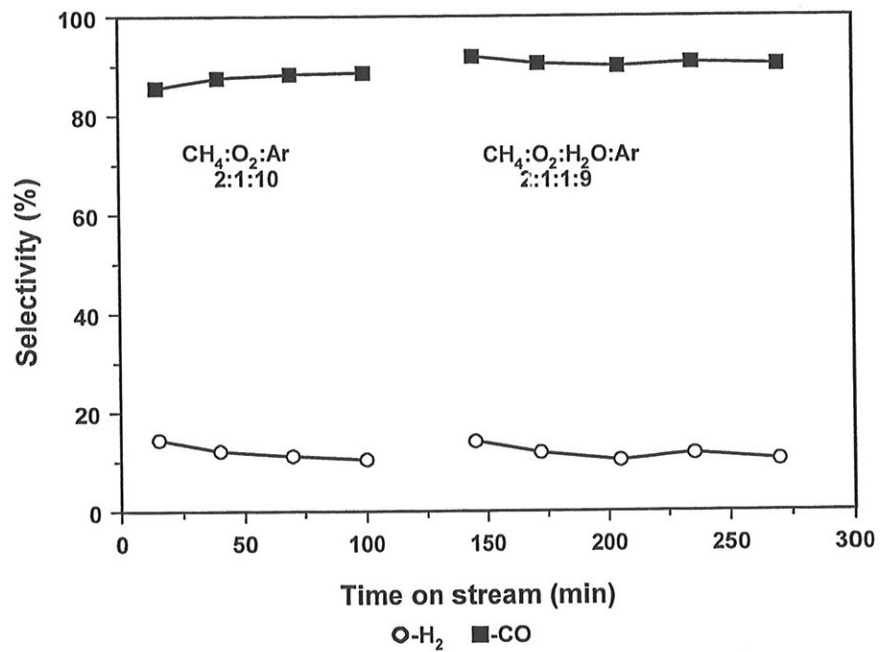
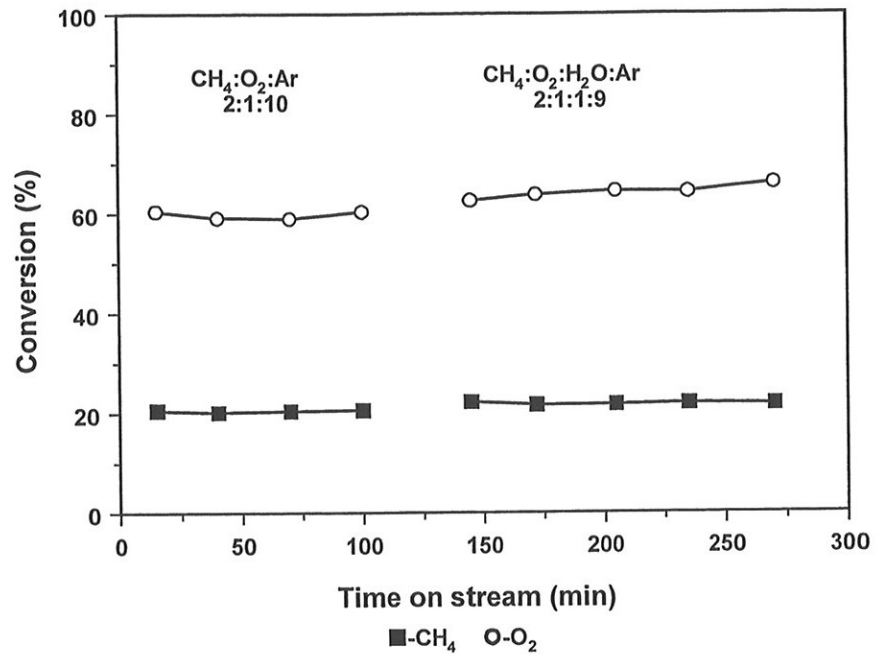


Figure 2: Conversion and selectivity before and after adding H<sub>2</sub>O to the feed over a Pt/10%Rh gauze at 1050 °C. The total flow rate is 2000 Nml/min.

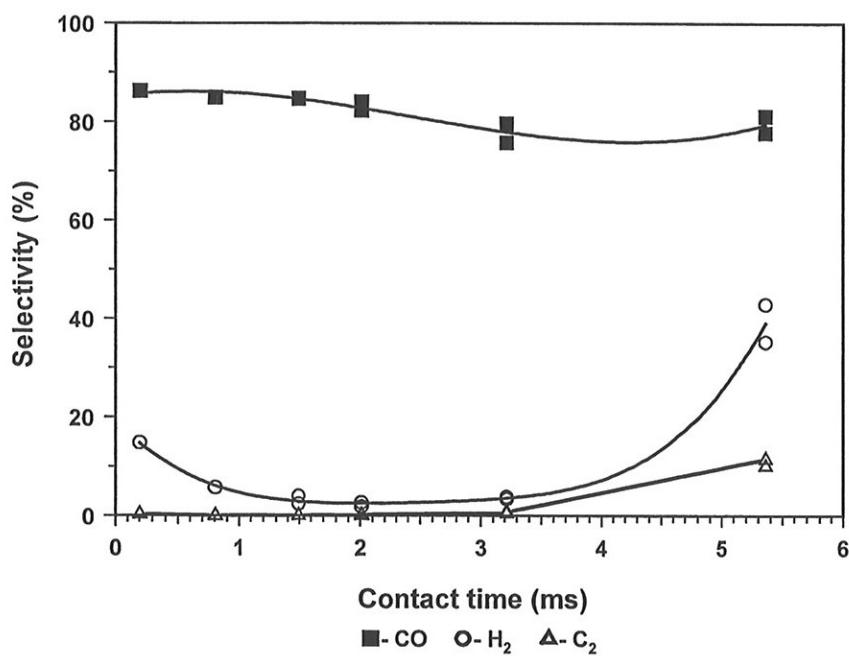
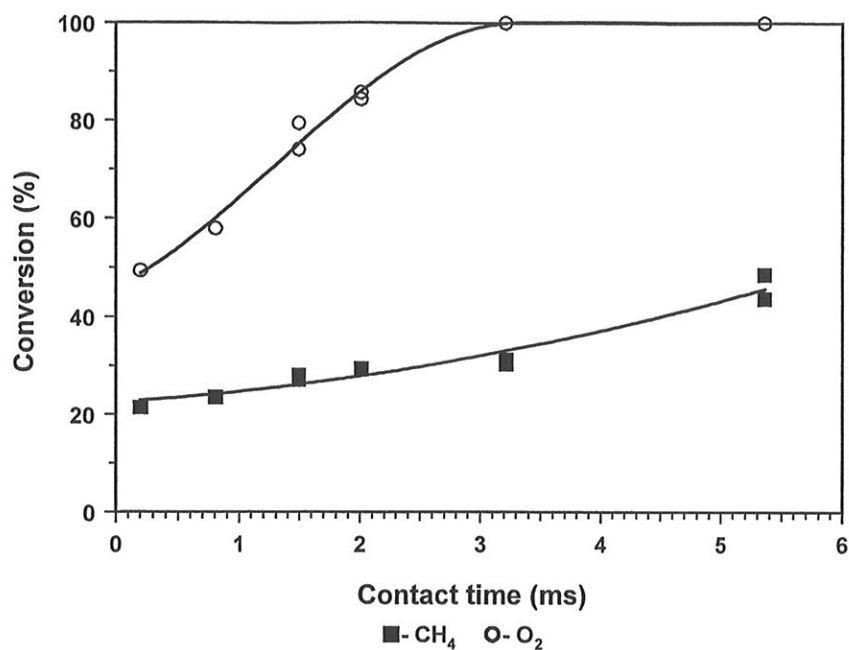


Figure 3: Conversion and selectivity over Pt/5%Rh gauzes at 1000 °C at various contact times. The feed composition is constant with a CH<sub>4</sub>:O<sub>2</sub>:Ar = 2:1:4. The flow rate is varied from 300 Nml/min to 2000 Nml/min. There are four gauzes on top of each other except from at  $\tau=0.21$  ms where only one gauze is applied.

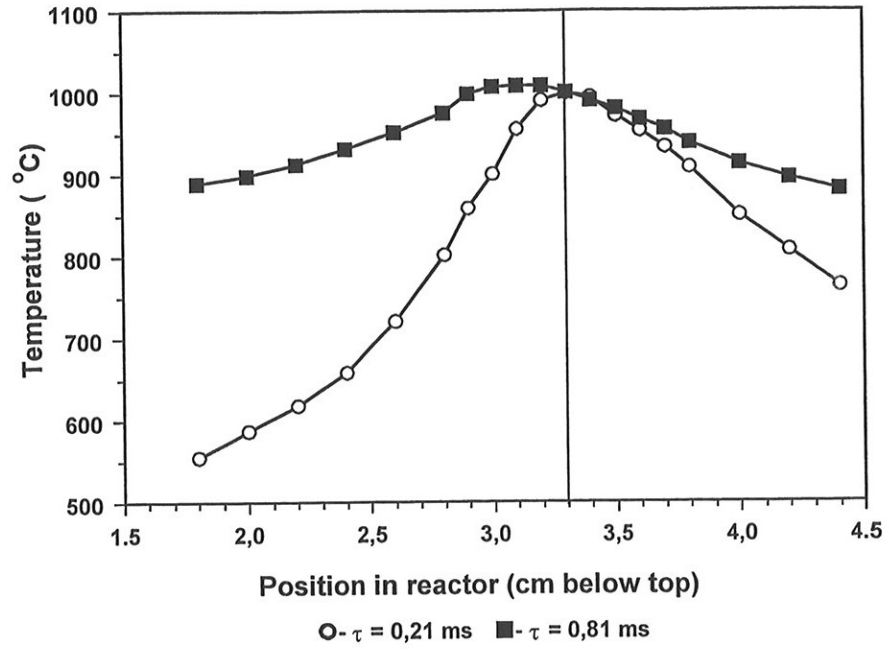


Figure 4: Temperature profiles over a Pt/5%Rh gauze at 1000 °C at different contact times. The feed composition is constant with  $CH_4:O_2:Ar = 2:1:4$ . The gauze position is marked as a vertical line in the figure 3,3 cm below the top of the reactor.





## Reactive Oxygen Species on Platinum Gauzes during Partial Oxidation of Methane into Synthesis Gas

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Platinum gauzes have been studied for the partial oxidation of methane in a high-temperature TAP-2 reactor between 800 and 1100°C. Two different oxidation procedures were used and the oxygen uptake has been measured. Alternating pulse experiments with oxygen and methane with various pulse intervals have revealed mechanistic information about the platinum catalyzed partial oxidation. It has been shown that carbon monoxide and hydrogen can be produced directly from methane and solid oxidized platinum. In the absence of gas phase oxygen, the maximum selectivities to carbon monoxide and hydrogen were 97 and 96%, respectively, at a methane conversion of 25%. At low surface oxygen concentrations, oxygen that is incorporated in the platinum bulk diffuses back to the surface to react with surface carbon to carbon monoxide. In that case the surface lifetimes of carbon monoxide and hydrogen are much shorter than the oxygen diffusion time and no consecutive oxidation reactions occur. The results of this study show that production of synthesis gas with high yields is possible by a direct route. © 2000 Academic Press

**Key Words:** partial oxidation; methane; synthesis gas; TAP; platinum; gauzes; bulk oxygen.

### INTRODUCTION

Partial oxidation of methane is an attractive way of producing synthesis gas (1–3). The partial oxidation of methane to synthesis gas can proceed through two routes: (i) indirectly, by total combustion into water and carbon dioxide and subsequent reforming of methane, and (ii) directly, by partial oxidation into hydrogen and carbon monoxide without going through reforming reactions. It has been shown that, under certain conditions and over certain catalysts, carbon monoxide and hydrogen are indeed primary products of the methane oxidation (4–10). This strongly depends on the availability of oxygen and oxygen–surface bond strengths (9). The problem with the industrial imple-

mentation of synthesis gas production through this route is that the primary products are more reactive for further oxidation to water and carbon dioxide with active oxygen surface species than the reactant methane (10). This limits the possible yields of synthesis gas production with methane and oxygen both present in the gas phase without going through reforming. Therefore, recent research on the direct partial oxidation has been directed toward reactions between methane and solid oxygen carriers such as for example CeO<sub>2</sub> (11). The idea is that oxygen supplied from a solid phase is less reactive than oxygen supplied from the gas phase.

In order to address the key question about the nature of selective and nonselective oxygen species, a study of the partial oxidation of methane over platinum gauzes was carried out in a new high-temperature TAP-2 reactor. A few studies report on TAP experiments for the partial oxidation of methane (4, 5, 9, 12–15). In most of them rhodium-based catalysts were used. Only two studies report on platinum catalysts (4, 14). Mallens *et al.* (4) distinguished three different types of oxygen, each being involved in a specific step in the reaction network. Soick *et al.* (14) carried out a kinetic analysis of the adsorption of methane, carbon monoxide and carbon dioxide over a Pt/MgO catalyst. No further information on the reaction mechanism has been reported. In the present study platinum gauzes are used which provide a unique catalyst because of the extremely short length of the catalytic zone. Moreover, due to the low dispersion of these gauzes the number of platinum surface atoms is equal to or lower than the number of methane molecules per pulse. This avoids gradients in the concentrations of adsorbed species along the catalyst layer which is usually the case in TAP experiments and which can complicate the interpretation of the data. The objective of this study is to clarify the reaction mechanism of the partial oxidation of methane at short contact times over platinum and at high temperatures (800–1100°C). The current study focuses on the different forms of oxygen species and their specific role in the mechanism.

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## EXPERIMENTAL

Woven platinum gauzes (supplied by K. A. Rasmussen, Norway) were used as catalysts. The wires have a diameter of 90  $\mu\text{m}$ , giving gauzes of 256 meshes/cm<sup>2</sup>. One single gauze (70–80 mg) is put in the reactor. The TAP-2 reactor is described elsewhere (16). For these experiments a new high temperature reactor was constructed that allows catalyst temperatures above 1000°C. The high temperature reactor is a 9.0-cm-high quartz cylinder with an inner diameter of 14 mm. The quartz tube is held between two stainless steel flanges. Two water-cooled viton O-rings are used as seals. A large temperature gradient exists along the reactor axis. However, a zone of about 1 cm is uniform in temperature. The reactor is filled with quartz particles (0.2–0.3 mm) in which the gauze is placed about 4.0 cm above the reactor exit. A thermocouple is placed very close to the gauze inside the reactor.

The total number of Pt atoms in the reactor amounts to 0.5 mmol. The number of surface Pt atoms in the reactor has been estimated to be 10 nmol using data from (17) corrected for the different gauze diameters. The number of methane or oxygen molecules admitted per pulse (~20–60 nmol) is higher than the number of active sites in the reactor (10 nmol). This implies that the reactant pulses largely influence the surface coverage. The alternating pulse experiments were conducted in the following way: oxygen was injected at  $t=0$  s, and then methane was injected at a later time, referred to as the pulse interval (between 0.05 and 3.0 s). The oxygen/methane ratio was approximately 1. The pulse size was always verified to be small enough to ensure Knudsen diffusion. The catalyst was prereduced in flowing hydrogen for 30 min at 900°C.

## RESULTS

A first experiment was carried out by pulsing methane and oxygen simultaneously over a reduced catalyst at 1000°C. In Fig. 1 the conversions and yields are shown for the reactants and products as a function of the pulse number. All the oxygen is consumed on the first pulse followed by an almost linear decrease in the oxygen conversion until it levels out around 90 pulses. During the first 70 pulses the methane conversion is rather low (~10%) and hardly any products are observed. During this time the baseline at mass 2 increased slowly, indicating the cracking of methane with a slow formation of hydrogen. At the time the oxygen conversion reaches a minimum (90–110 pulses) the conversion of methane increases rapidly and the production of all products is observed. At this point the oxygen conversion increases slightly and the signals of all reactants and products remain stable over a long period of time. In all other experiments the catalyst was always preoxidized.

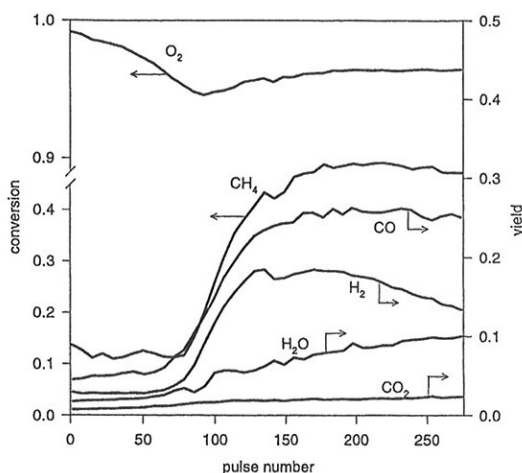


FIG. 1. Conversions and selectivities during simultaneous pulsing of CH<sub>4</sub> and O<sub>2</sub> over a prereduced Pt gauze at 1000°C.

Two methods of oxidation were used and the uptake was measured in both cases:

- By a steady flow of oxygen at 1 bar and at 900°C.
- By pulsing oxygen on the prereduced catalyst while keeping the reactor under vacuum at 900°C. Oxygen was pulsed over the catalyst until the oxygen signal was stable.

Under vacuum conditions surface oxygen readily desorbs from the platinum. This was observed by a small additional uptake of oxygen (typical 20–50% of a single pulse) after a few minutes under vacuum. The oxygen uptakes in the two cases are compared in Table 1. The amount of oxygen uptake differs significantly for the two pretreatments, but is in both cases far beyond the amount that corresponds to an adsorbed monolayer (assuming a Pt:O = 1:1 stoichiometry). The two different oxidation procedures did not result in any difference in catalyst performance for the oxidation of methane.

The partial oxidation of methane was further studied by using alternating pulses of oxygen and methane over pre-oxidized platinum at 900°C at vacuum conditions. The only varied parameter was the time between the oxygen and the methane pulses (0.05–2.5 s). Figure 2 shows the calibrated

TABLE 1  
Oxygen Uptake for the Different Applied Procedures  
on a Prereduced Pt Gauze at 900°C

	Steady flow of O <sub>2</sub>	Pulses of O <sub>2</sub>
O uptake	$1.3 \times 10^{20}$ (molec.)	$1 \times 10^{18}$ (molec.)
O/Pt <sub>total</sub>	0.43	0.003
O/Pt <sub>surface</sub>	26000	200



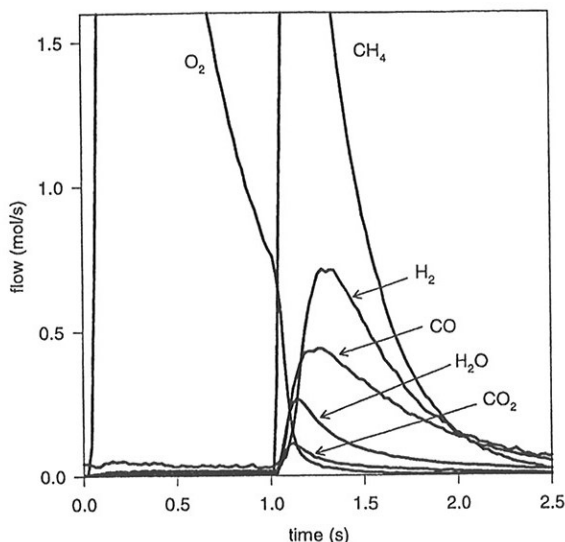


FIG. 2. Transient responses of reactants and products during an alternating  $O_2$ - $CH_4$  pulse experiment over a preoxidized Pt gauze at  $900^\circ C$  with a pulse spacing of 1.0 s.

reactant and product responses after an oxygen pulse at  $t=0$  s and a methane pulse at  $t=1.0$  s. This figure clearly shows that when methane is injected, the oxygen signal rapidly drops down to zero. The carbon monoxide, carbon dioxide and water signals appear immediately. When the oxygen signal has almost disappeared, the carbon dioxide and water signals start to decrease. The carbon monoxide signal continues to increase, and finally the hydrogen signal appears. The hydrogen production is clearly delayed until the oxygen signal is almost zero. The carbon monoxide and hydrogen signals reach their maxima at about the same time, long after the carbon dioxide and water. At this time the methane signal is also rapidly decreasing. The decay of the carbon monoxide curve is rather slow and it tails for more than 2 s.

Figure 3 shows the conversion of methane and the selectivities to hydrogen and carbon monoxide as a function of the pulse interval. The methane conversion decreases from approximately 35 to 25%, but the hydrogen and carbon monoxide selectivities are strongly increasing with increasing pulse interval from 25 and 12% to 96 and 97%, respectively. At a pulse interval of about 2 s, the conversion and selectivity reach steady values.

Experiments using alternating pulses of oxygen and carbon monoxide over a preoxidized catalyst showed very low activity for the oxidation of carbon monoxide at pulse interval of 2 s. The carbon monoxide conversion was about 7%. A similar experiment with oxygen and hydrogen showed a hydrogen conversion of 2%.

To assess the extent of the reaction between carbon dioxide and methane, another similar alternating pulse experiment was carried out by pulsing oxygen followed 2 s later by a pulse of a mixture of methane (95%) + carbon dioxide (5%). No conversion of carbon dioxide was observed and the methane conversion was unaffected by the presence of carbon dioxide.

Alternating pulse experiments similar to those in Fig. 2 were carried out with  $^{18}O_2$  to further investigate the reactivity of the different oxygen species. The platinum gauze was preoxidized with pulses of  $^{16}O_2$ . For the alternating pulse experiments  $^{18}O_2$  was used on the first pulse. Scrambling into  $^{16}O^{18}O$  (15 to 25%) was observed in all experiments. No significant amounts  $^{16}O_2$  were observed in these experiments.

Two different pulse responses of  $C^{16}O$  and  $C^{18}O$  with two distinct time scales were observed for all pulse intervals as shown in Fig. 4 (curves 1 and 4, respectively). The response of  $C^{16}O$  is significantly slower than the response of  $C^{18}O$  and shows a large tailing. The selectivities of  $C^{16}O$  and  $C^{18}O$  as a function of the pulse interval are shown in Table 2. There is a clear increase toward  $C^{16}O$  with increasing pulse interval which slowly levels off at intervals larger than 1 s. Concerning the carbon dioxide formation,  $C^{18}O_2$  is formed first, followed a little later by  $C^{16}O^{18}O$  and at last a slow formation of  $C^{16}O_2$  is observed. The relative amounts of the  $C^{18}O^{18}O$ ,  $C^{16}O^{18}O$ , and  $C^{16}O_2$  were found to be 2:2:1.

The rate of adsorption of carbon monoxide was investigated by pulsing carbon monoxide over a reduced catalyst.

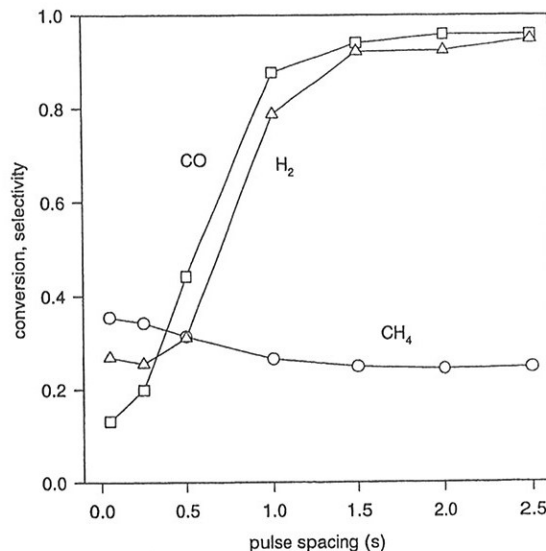


FIG. 3. Conversion of methane and selectivity to synthesis gas as a function of the pulse spacing between  $O_2$  and  $CH_4$  over a preoxidized Pt gauze at  $900^\circ C$ .

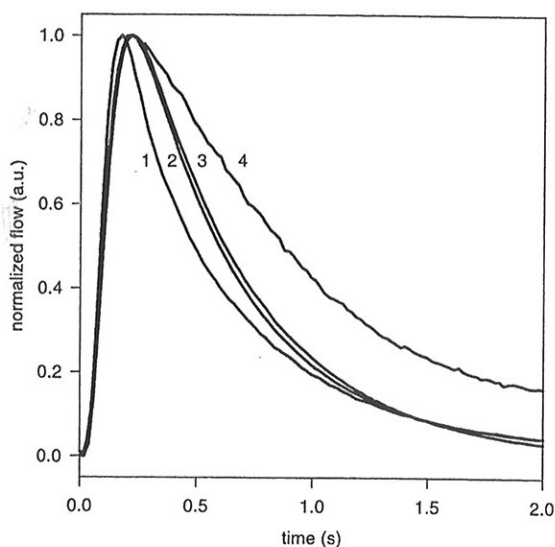


FIG. 4. Height normalized carbon monoxide and argon signals at 900°C. (1) The  $C^{18}O$  transient response from alternating pulses of  $^{18}O_2$  followed by  $CH_4$  at  $t=0.1$  s over a  $^{16}O_2$  preoxidized Pt gauze. (2) Transient response of argon. (3) The CO transient response from a pulse of CO over a pre-reduced Pt gauze. (4) The  $C^{16}O$  transient response from alternating pulses of  $^{18}O_2$  followed by  $CH_4$  at  $t=0.1$  s over a  $^{16}O_2$  preoxidized Pt gauze.

Its response is shown as curve 3 in Fig. 4. The shape of the response of a pulse of carbon monoxide (curve 3) is rather close to an inert argon pulse shape (curve 2) and does not show any tailing.

The same trend of results as described above was observed in the temperature interval between 800 and 1100°C.

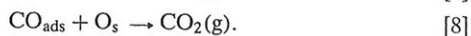
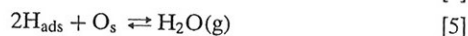
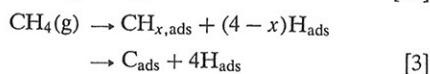
## DISCUSSION

On the basis of the current data the following reaction scheme is proposed:

TABLE 2

Product Distribution from a Pulse of  $^{18}O_2$  Followed by a Pulse of Methane over a Preoxidized ( $^{16}O$ ) Pt Gauze at 900°C

Time interval between $^{18}O_2$ and $CH_4$ (s)	$X_{CH_4}$	$S_{C^{18}O}$	$S_{C^{16}O}$	$\Sigma S_{CO}$
0.1	0.35	0.14	0.02	0.16
0.5	0.31	0.26	0.18	0.44
1.0	0.26	0.39	0.49	0.88
2.0	0.24	0.34	0.62	0.96
3.0	0.24	0.31	0.65	0.96



The oxygen uptake during the preoxidation of the catalyst was much larger than an adsorbed monolayer for both oxidation procedures (Table 1). This means that, in addition to a dissociative adsorption of oxygen on the platinum surface step [1], there is an uptake of oxygen by bulk platinum as described by step [2]. Oxygen uptake in the same order of magnitude has previously been reported during oxygen pulsing over a platinum sponge in the TAP reactor (4). In a series of simultaneous pulses of oxygen and methane over a reduced platinum gauze (Fig. 1), oxygen is initially adsorbed at the platinum surface, followed by diffusion into the bulk rather than reacting with surface carbon. This suggests that surface oxygen is rapidly converted to bulk oxygen through step [2a] to oxidize more than the surface platinum layer. Then a stabilized oxidized state is reached defining the working platinum catalyst under the conditions applied in this study.

The observed oxygen scrambling into  $^{16}O^{18}O$  on pulsing  $^{18}O_2$  over a gauze saturated in bulk  $^{16}O$  supports that  $^{18}O_2$  chemisorbs reversibly and dissociatively on platinum (reaction [1]) and that there is an exchange between the bulk and the surface (steps [2a] and [2b]).

The lack of tailing on the methane pulse indicates an irreversible methane adsorption (step [3]). The extent of the dissociation can not be directly deduced from these data. However, the marked tailing on the hydrogen signal as shown in Fig. 2 suggests that the partly dehydrogenated carbon species ( $CH_3$ ,  $CH_2$ , or  $CH$ ) has a significant surface lifetime. On subsequent oxygen pulses small amounts of carbon monoxide and carbon dioxide were observed, but no significant amounts of water, indicating that step [3] is completed within a few seconds.

The adsorbed hydrogen atoms can either combine through step [4] into hydrogen gas or can react with surface oxygen to form water (step [5]). The pulse response of hydrogen over oxidized platinum indicated that its dissociative adsorption is fast and reversible. A similar analysis showed a reversible adsorption of water.

Comparison of the responses of  $C^{18}O$  and  $C^{16}O$  (Fig. 4, curves 1 and 4) clearly shows the rapid formation of the

former, while the production of the latter continues for several seconds. Therefore the reaction between surface carbon and  $^{18}\text{O}$ , mainly located on the surface as it was produced from a recent pulse of gaseous  $^{18}\text{O}_2$ , is relatively fast, whereas the reaction of surface carbon and  $^{16}\text{O}$ , mainly originating from the bulk, is considerably slower but can continue for a long time due to the large quantities of bulk  $^{16}\text{O}$  available. Surface oxygen is rapidly depleted once the gas phase oxygen concentration goes to zero due to its desorption under vacuum conditions. The difference in rate between the formation of  $\text{C}^{18}\text{O}$  and  $\text{C}^{16}\text{O}$  suggests a diffusion of  $^{16}\text{O}$  from the bulk to the surface (step [2b]), typically a slow process. An estimate for the time of oxygen diffusion is given by the difference between the average residence times of  $\text{C}^{16}\text{O}$  and  $\text{C}^{18}\text{O}$  and amounts to 0.3 s at  $900^\circ\text{C}$ . An order of magnitude diffusion coefficient of  $10^{-19} \text{ m}^2 \text{ s}^{-1}$  can be calculated if a diffusion distance of one platinum monolayer is assumed. This stems from the idea that  $^{16}\text{O}$ , which is most likely to react, is located just underneath the surface. The incorporation of oxygen into the platinum bulk is an activated process since at relatively low temperatures the amount of oxygen uptake corresponds well with the number of surface platinum atoms.

The ratio  $\text{C}^{18}\text{O}/\text{C}^{16}\text{O}$  decreases with increasing pulse interval (Table 2). The residence time of surface oxygen is short due to the fast desorption rate at high temperatures under vacuum conditions. Increasing the pulse interval decreases the concentration of surface oxygen at the time of the injection of methane. Bulk oxygen is much more stable at these conditions, indicated by the negligible oxygen uptake that was observed after keeping an oxidized gauze under vacuum. So, by increasing the pulse interval, the diffusion of bulk oxygen and the recombination/desorption of  $^{18}\text{O}$  are increasing, resulting in an increase in the surface concentration of  $^{16}\text{O}$  at the expenses of  $^{18}\text{O}$ .

The reactivity of bulk oxygen toward carbon monoxide and hydrogen is very low. This can be concluded from pulsing  $\text{CO}$  or  $\text{H}_2$  over oxidized platinum without gas phase oxygen present. This resulted in very low conversions of approximately 2–5%, while 30% conversion was obtained for methane under identical conditions. In contrast the reactivity of surface oxygen toward carbon monoxide and hydrogen is very high since at short pulse intervals between  $\text{O}_2$  and  $\text{CO}$  or  $\text{H}_2$ , corresponding to high concentrations of surface oxygen, an almost complete conversion of carbon monoxide or hydrogen was observed. These conclusions are also supported by the labeled carbon dioxide product distribution.  $\text{C}^{18}\text{O}_2$  is the first product, due to the fast reaction between surface carbon and surface  $^{18}\text{O}$  followed by the fast reaction between adsorbed  $\text{C}^{18}\text{O}$  and surface  $^{18}\text{O}$ .  $\text{C}^{18}\text{O}^{16}\text{O}$  follows a little later in time, due to the slower formation of  $\text{C}^{16}\text{O}$ . Very little  $\text{C}^{16}\text{O}^{16}\text{O}$  is formed because of the low probability of the reaction between  $^{16}\text{O}$  originating from the bulk and  $\text{C}^{16}\text{O}$ .

A similar analysis for the formation of water was unfortunately impossible due to the overlap between the fragments of all (labeled) reactants and products and those of (labeled) water.

All this agrees well with the results of Lauterbach *et al.* (18), who investigated the properties of oxygen on Pt(111) surfaces by photoemission electron microscopy. They observed the diffusion of oxygen into the bulk platinum and referred to this species as subsurface oxygen. A negligible reactivity of subsurface oxygen with either carbon monoxide or hydrogen was observed. From their experiments as a function of temperature they estimated an activation energy of  $63 \pm 21 \text{ kJ mol}^{-1}$  for the incorporation of oxygen into the platinum bulk.

The pulse response of carbon dioxide was very close to the response of argon, indicating that its adsorption can be neglected and that the reverse reaction of step (8) can be ignored. This can be understood from the fact that under the applied conditions the contact time of carbon dioxide is too short and the oxygen surface concentration is too large for any significant reaction of carbon dioxide to occur.

The maxima of the carbon dioxide and water shown in Fig. 2 are observed prior to those of carbon monoxide and hydrogen. Moreover, the responses of carbon dioxide and water are quite narrow. In contrast to previous interpretations (12, 13) this does not imply that carbon monoxide and hydrogen arises from secondary reforming reactions involving carbon dioxide and water. Due to the high concentration of surface oxygen, initially all the methane is oxidized to carbon dioxide and water. When the surface oxygen is depleted and no more gas phase oxygen is present to replenish the surface, the remaining surface carbon is selectively converted into carbon monoxide by the reaction with oxygen that is diffusing from the bulk to the surface. Therefore carbon monoxide and hydrogen exit the reactor after carbon dioxide and water.

The above developed reaction mechanism explains well the change in selectivity as a function of pulse interval as reported in Fig. 3. As the concentration of surface oxygen decreases with increasing pulse interval the consecutive oxidation of carbon monoxide and hydrogen diminishes rapidly, resulting in very high selectivities. The product distribution is completely determined by the surface oxygen concentration. At high surface oxygen concentrations the consecutive reactions of carbon monoxide and hydrogen are much faster than their corresponding desorption steps. However, at low surface oxygen concentrations the diffusion of bulk oxygen is slow compared to the residence time of carbon monoxide and hydrogen and negligible complete oxidation occurs. The surface lifetime of carbon is much longer and the diffusion of oxygen becomes then rate determining for the formation of carbon monoxide. The desorption of oxygen originating from the bulk was found to be rather slow

under TAP conditions which is due to the slow diffusion rate of bulk oxygen.

Figure 3 shows that the methane conversion is above 35% at high surface oxygen concentrations whereas it approaches 25% when the surface is depleted of oxygen. In line with the above discussion, that difference could arise from the fact that at low oxygen surface coverage, the methane conversion is limited by the oxygen diffusion from the bulk to the surface while at high oxygen surface coverage, another step, faster than bulk oxygen diffusion, would limit the overall process. Since the number of gas molecules is higher than the number of platinum surface atoms and adsorption can be considered as very fast compared to the surface reaction, the number of adsorption sites determines the methane conversion. Or in the form of an equation:

$$X = \frac{N_{\text{sites}}}{N_{\text{CH}_4}}$$

At low surface oxygen concentrations the catalytic cycle of the site (the time required for a site to convert a methane molecule) is low due to the slow diffusion of oxygen. By the time the site has become available for reaction, the methane gas concentration has become zero. On the contrary, at high surface oxygen concentrations the reoxidation of surface carbon is faster than the diffusion time of gas phase methane and the site is again available for methane adsorption, resulting in a higher methane conversion. Thus the ratio of the conversions at high and at low surface oxygen concentrations shows that at a conversion of 0.35 the same sites are working 1.4 times more than at a conversion of 0.25.

The residence time of methane in the gas phase inside the catalyst zone for a thin catalyst layers can be calculated according to (20)

$$\tau = \frac{\varepsilon \Delta L L_2}{D}$$

where  $\tau$  is the average residence time (s),  $\varepsilon$  is the bed porosity ( $\text{m}^3 \text{m}^{-3}$ ),  $\Delta L$  the catalyst zone length (m),  $L_2$  the inert zone after the catalyst (m), and  $D$  the Knudsen diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ). For the current reactor configuration a residence time for methane of 0.5 ms was calculated. The apparent rate constant for the oxidation of surface carbon at high surface oxygen concentrations is thus  $>2000 \text{ s}^{-1}$ .

As mentioned in the introduction, Mallens *et al.* (4) reported on the existence of three different kinds of oxygen species on a platinum sponge under vacuum conditions at 800°C. They referred to these three species as platinum oxide, dissolved oxygen, and chemisorbed oxygen. According to their reaction network direct formation of carbon monoxide occurs via the oxygen present as platinum oxide and dissolved oxygen converts adsorbed carbon and hydrogen into carbon dioxide and water. The consecutive oxidation of carbon monoxide and hydrogen into carbon

dioxide and water involves chemisorbed oxygen. The results presented in this study did not indicate the existence of dissolved oxygen. After an oxidation of the platinum gauze by a flow of oxygen, no further oxygen uptake was observed during a multipulse experiment, as was the case in the study by Mallens *et al.* The quantities of dissolved oxygen reported were rather low and the distinction between dissolved oxygen and platinum oxide is not very clear. The small amounts of additional oxygen uptake that was observed after exposure of an oxidized catalyst to vacuum conditions in this study is believed to correspond to a slow desorption of bulk oxygen and not to the formation of a different type of oxygen.

## CONCLUSION

The partial oxidation of methane over platinum gauzes in the TAP reactor takes place through a direct path to carbon monoxide and hydrogen. At high temperatures oxidation of platinum proceeds beyond a surface layer, well into the bulk phase. The product distribution is determined by the surface oxygen concentration. In the presence of gas phase oxygen the surface oxygen concentration is very high and consecutive oxidation of carbon monoxide and hydrogen takes place. In the absence of gas phase oxygen, the diffusion of oxygen from the bulk toward the surface is slower than the desorption of carbon monoxide and hydrogen and syngas is produced with high selectivities. Therefore a strict control of the surface oxygen reactivity is a prerequisite for any highly selective direct oxidation process to syngas over platinum. This can be attained by reducing either its concentration or its mobility. The former requires a process that avoids the simultaneous presence of methane and oxygen in the gas phase. This could be accomplished by nonstationary reactor operation with an alternating feed of methane and oxygen. Preliminary experiments still in progress in the laboratory already demonstrated the validity of that concept which has also been investigated by other research groups over different metal catalysts (21, 11). The oxygen mobility can be modified by adding a different metal to the platinum. This is the case for platinum rhodium for which high syngas selectivities have been reported (22).

## ACKNOWLEDGMENTS

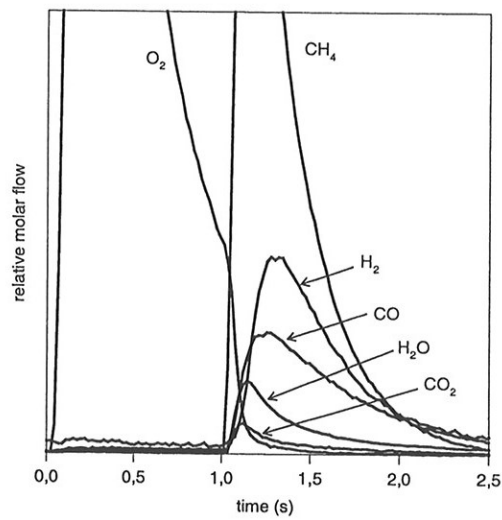
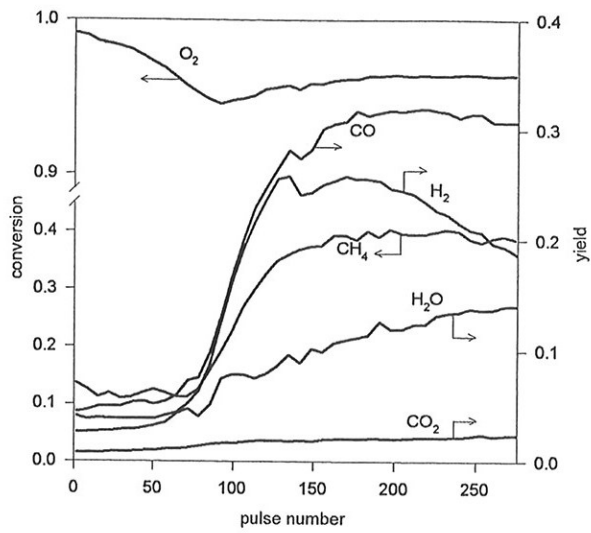
The financial support from the Norwegian Research Council is greatly acknowledged.

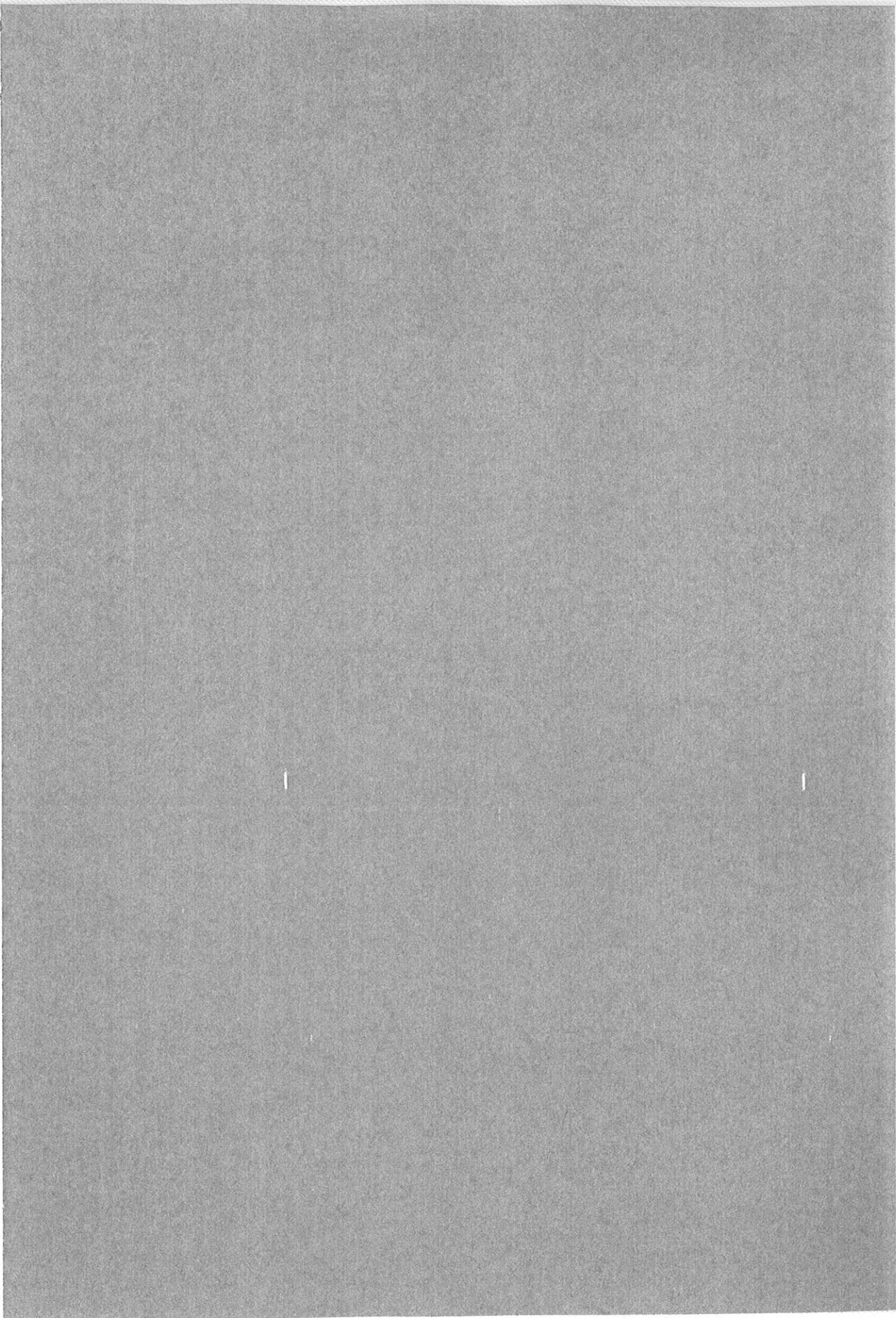
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**Errata:** Figures 1 and 2 with correct axis titles and curve notations:





## Partial oxidation of methane to synthesis gas:

### Elimination of gas phase oxygen

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Running title: "Partial oxidation of methane to synthesis gas: Elimination of gas phase oxygen"



**Keywords:** Partial oxidation; methane; synthesis gas; cerium oxide; platinum, rhodium

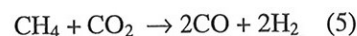
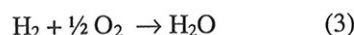
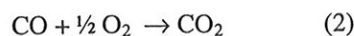
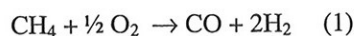
### **Abstract**

The reaction between methane and cerium oxide to produce syngas has been studied at 700 °C in a pulse apparatus. The cerium oxide was supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and promoted by reimpregnation with Pt or Rh. The promoters drastically enhanced the conversion of methane. TPR with hydrogen shows that Pt and Rh also lowered the temperature necessary to reduce the cerium oxide. Studies of the reaction between methane and promoted cerium oxide showed that the selectivity to syngas depended on the degree of reduction of the cerium oxide. The promoters also led to some carbon formation. Regeneration of the reduced oxide was studied both with oxygen and carbon dioxide.

### **Introduction**

Partial oxidation of methane is an attractive way to produce synthesis gas [1]. The partial oxidation of methane to synthesis gas can proceed through two routes: 1) Indirectly through combustion (reactions 1+2+3) followed by subsequent reforming (reactions 4 and 5) of methane and 2) through the direct reaction between methane and oxygen (reaction 1). It has been shown that under certain conditions over certain catalysts, the direct formation of synthesis gas from methane and oxygen is possible [2-5]. This strongly depends on the availability of oxygen on the catalyst surface and on the oxygen-surface bond-strength [2]. The problem with industrial implementation of synthesis gas production through this route is the reactivity between oxygen and the primary products carbon monoxide and hydrogen

to form carbon dioxide and water [5]. This limits the possible yields of synthesis gas from the direct reaction between methane and oxygen at lower temperatures.



Recent research has been directed towards reaction between methane and solid oxygen carriers. A recent study has shown that oxygen in solid oxidized platinum has high activity for methane oxidation to syngas and at the same time a low activity for oxidation of hydrogen and carbon monoxide [4]. Oxygen bound or dissolved in a solid platinum matrix was found to be less reactive than oxygen supplied from a gas phase and thereby largely increasing the syngas selectivity. This was proposed related to the diffusion rate of oxygen in platinum and the surface residence times of the reacting species. However, platinum is a rather expensive material and large volumes would be necessary if it was used only as an oxygen reservoir. Cerium oxide has been shown to have capacity to store and release oxygen in many applications [6-9]. Otsuka and coworkers [8,9] have studied the reaction between methane and cerium oxide and found that synthesis gas indeed can be formed. Physical mixing with platinum black had a large effect on the conversion of methane.

This study deals with the reaction between methane and cerium oxide promoted directly with platinum and rhodium. Reoxidation of the same materials with oxygen and carbon dioxide has also been studied. The carbon deposition during reaction with methane and the carbon removal with oxygen or carbon dioxide has been measured.

## Experimental

### *Catalyst preparation and characterization*

The materials were prepared by incipient wetness impregnation of about 20% CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> material was supplied by Alfa Aesar in pellets and crushed down to particles in the size 300-710  $\mu$ m. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with Ce(NO<sub>3</sub>)<sub>3</sub>\*6H<sub>2</sub>O dissolved in distilled water, dried at 150 °C and calcined in air at 600 °C for 10 h. The materials were reimpregnated with either 0.5 wt% Pt (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) or Rh (Rh(NO<sub>3</sub>)<sub>3</sub>) and calcined again in air at 600 °C for 10 h. Table 1 shows the BET surface areas of the samples before and after impregnation. Temperature programmed reduction (TPR) with H<sub>2</sub> (7% H<sub>2</sub> in Ar) was performed with a heating rate of 10 °C/min. Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were also studied to have reference peaks for Pt and Rh. X-ray diffraction was performed on the CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the Pt/CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and a sample of Pt/CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that had been studied in the reaction with methane and reoxidized in oxygen.

### *Reactor setup and experimental procedure*

Reactions with methane, oxygen and carbon dioxide over the various materials were carried out by injecting 0.25 Nml (10 micromoles) of reactant pulses into a steady flow of He (50 Nml/min) that passed over the material samples (0.5 g) which were placed inside an electrically heated quartz reactor. Downstream of the reactor, the He flowed through a packed Porapak Q column (2.1 m, ¼ inch) that was isothermal at 70 °C. At the exit of the column there were both a TCD detector and in certain cases a Gaslab 300 mass spectrometer. The total pressure in the reactor was always 1.8 bars. All lines downstream of the reactor were heated to avoid condensation upstream of the analytic tools. The reactor was a quartz tube with an inner diameter of 3 mm. This gave a linear gas velocity of 0.22

m/s at 700 °C (1.8 bars) and a contact time between the reactant gases and the material samples (void fraction 0.4) of about 0.26 s. Complete separation and analysis (12-15 minutes) of the products from a reactant pulse was allowed before a new pulse was introduced. The materials were studied in cycles of multiple pulses of oxygen and subsequently multiple pulses of methane. The materials were then reoxidized in a pulse series of oxygen or carbon dioxide before again starting new series of methane pulses. Carbon deposition was studied in the above-described procedure by measuring the formation of carbon oxides while pulsing oxygen over the used samples.

## Results and discussion

### *Characterization*

The TPR analysis is shown in Figure 1A-C. First the calcination temperature of the  $\text{Ce}(\text{NO}_3)_3$  impregnated  $\gamma\text{-Al}_2\text{O}_3$  was studied. Three samples calcined at 400, 500 and 600 °C for 10 h were analyzed and the resulting TPR patterns of the calcined samples are shown in Figure 1A. The sample calcined at 400 °C had some broad peaks below 500 °C. These peaks were smaller on the sample calcined at 500 °C, and were not present on the sample calcined at 600 °C. The TPR shown in curve 1A c) is also identical to TPR curves obtained from pure  $\text{CeO}_2$  in the literature [6, 9]. This showed that a calcination temperature of 600 °C was necessary to obtain complete decomposition of the cerium nitrate. The calcination temperature was therefore set to be 600 °C. Figure 1B shows the effect of adding platinum. The unpromoted 20 wt%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  showed no hydrogen consumption before the temperature reached 350 °C. The pure 0.5 wt%  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  had two peaks of hydrogen consumption at approximately 230 and 430 °C. The peaks were relatively small indicating that the amounts of hydrogen consumed were relatively low. In the cases where cerium oxide was present, as in the rest of the samples in Figure 1B, the

hydrogen consumption was several orders of magnitude greater. For the 0.5 wt% Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, the peaks were approximately at the same temperatures as for the 0.5wt% Pt/γ-Al<sub>2</sub>O<sub>3</sub>, but the areas underneath them were much larger. This indicates that the Pt largely affected the reduction of cerium oxide. There was also an effect of the Pt weight loading. The temperature necessary for reduction decreased with increasing weight loading of Pt. The low temperature peak of Pt was most affected and displaced from 280 to about 160 °C with an increasing weight loading from 0.25% to 1.0%. The shoulder of the low temperature peak switched from being below to above the main peak with increasing Pt loading. Peak shoulders and peak displacements with variations in the Pt loading on CeO<sub>2</sub> have also been reported in the literature [6]. Figure 1C shows the reduction of the calcined rhodium catalyst with and without cerium oxide. The areas underneath the Rh-peaks were also here greatly affected by the cerium oxide. The peak of Rh/γ-Al<sub>2</sub>O<sub>3</sub> at 210 °C was much broader was displaced about 50 °C higher in the presence of CeO<sub>2</sub>.

The BET surface area measurements in Table 1 showed that the pure γ-Al<sub>2</sub>O<sub>3</sub> support lost some surface area when impregnated with 20% cerium oxide. Reimpregnating the CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> with the promoters Pt or Rh did not affect the surface area of the material significantly.

The X-ray diffractograms of the material samples are shown in Figure 2. The CeO<sub>2</sub> and the γ-Al<sub>2</sub>O<sub>3</sub> phases were easily identified [10,11]. No unassigned peaks were discovered. In addition, the diffractogram shows that the peaks were relatively broad. This means that the crystal planes corresponding with the peaks were relatively small. This was not unexpected, considering the porous nature of the γ-Al<sub>2</sub>O<sub>3</sub>. As expected, the X-ray diffractogram of Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was identical to the one of pure CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. As little as 0.5 wt% Pt is invisible by XRD, but this shows that the CeO<sub>2</sub> phase was not to a

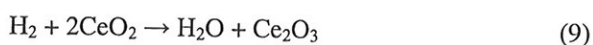
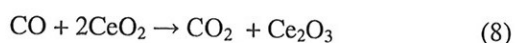
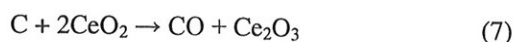
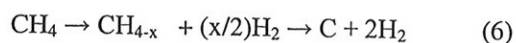
detectable degree affected by the presence of Pt. The diffractogram of the used and reoxidized sample of Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was identical to the fresh sample indicating no permanent structural change of the oxide after being treated in cycles with methane and oxygen.

#### *Partial oxidation of methane*

The reduction of the oxidized materials with methane was studied at 700 °C. Bar charts were chosen to represent the results from these experiments for two major reasons: Firstly, the material balance is very well visualized. The amount of methane injected was 10 micromoles. On basis of the carbon and hydrogen balance, the sums of the different product yields therefore easily show if there was any accumulation in the reactor. This was the case in all the experiments. Secondly, the bar charts illustrate well the discontinuous nature of the experiments. Methane was injected as separate pulses and not as a continuous flow.

Figures 3 and 4 show the products from 28 pulses of methane injected over CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, Rh/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The hydrogen and water in Figure 4 were detected by the mass spectrometer. These materials were fresh after the calcination. They had in addition been pretreated *in situ* with pulses of oxygen at 700 °C to ensure complete oxidation. There was no reoxidation in between the pulses of methane. The absolute first pulses of methane yielded mostly carbon dioxide with all the materials. For the unpromoted cerium oxide, the conversion of methane became low after a few pulses. However, there were drastic promoter effects from both Rh and Pt. The first pulses gave full conversion of methane and the yield shifted from carbon dioxide towards carbon monoxide. The yield of carbon monoxide was higher with Pt than with Rh. Significant methane slip occurred after 20 pulses with Rh and 14 with Pt as promoter, whereas

methane slip occurred after only one methane pulse over the unpromoted  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . For the promoted materials it is important to note that after a few pulses the sum of methane, carbon monoxide and carbon dioxide did not add up to the 10 micromoles that was the amount of methane injected. The carbon balance therefore strongly indicates that the rest was accumulated in the reactor as some form of carbon. Reactions 6-9 describe the formation of carbon and hydrogen and the oxidation to gaseous products by the cerium oxide.



The carbon balance shows that more carbon was formed with Rh as promoter than with Pt. It is also very interesting to observe the very low carbon deposition on the unpromoted cerium oxide. This indicates that reaction (6) is catalyzed by the noble metal promoters. The MS analysis of hydrogen and water in Figure 4 shows that from the absolute first pulse of methane, very little water and no hydrogen came out of the reactor. Cold spots downstream of the reactor were avoided by thorough heating of all lines. The high selectivity towards carbon dioxide in the same first pulse made it reasonable to expect high selectivity towards water at the same time. Since almost no hydrogen containing molecules came out, this must in some way have accumulated on the material in the reactor. This accumulation occurred at a point when the material was relatively fresh and near fully oxidized. Hydrogen accumulation as hydroxyl groups on the ceria surface could explain this accumulation. Hydroxyls could be formed through hydrogen spillover from Pt. Heterolytic splitting of methane on ceria seems less probable as indicated by the higher

activity of the material in presence of a noble metal. Hydroxylation of the ceria surface by water formed in the oxidation reaction is also a possibility.

After the 28 pulses of methane (Fig. 4), the oxygen quantity removed from the material corresponded to a stoichiometric oxide formula of  $\text{CeO}_{1.6}$ . This indicates a one-step reduction mechanism of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , which would give  $\text{CeO}_{1.5}$ . Otsuka and coworkers [8] observed a similar degree of reduction. The above experiment also showed that in the reaction between methane and promoted ceria, the selectivity towards carbon monoxide and hydrogen strongly depended on the degree of oxidation of the material. High selectivity was obtained when the most reactive oxygen had been removed as was the case after approximately 50 micromoles of methane.

In order to be able to discuss the phenomena that take place in this reactor it is necessary to have a good idea of the morphology of the material and the dynamic processes involved. The XRD peaks of the ceria were not affected by the presence of Pt or Rh. The XRD also clearly identified the phase  $\text{CeO}_2$ . Since the platinum and rhodium were impregnated on the  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  after the first calcination, it is reasonable to believe that these metals exist as separate crystallites on top of the cerium oxide phase. The interpretation of the results must therefore take into account that the surface is heterogeneous and consists of two distinctly different phases; one as cerium oxide and one as platinum or rhodium in some oxidized or reduced state. Both TPR and the pulse experiments with methane show large promoter effects. The  $\text{H}_2$ -TPR results show that the promoters affect the reduction temperature of the cerium oxide. Platinum and rhodium also drastically enhanced the conversion of methane in the pulse experiments. Hence, there is no doubt that these metals must take an active part in the conversion. If the metals are relatively small particles on a large quantity of cerium oxide, the metals are in contact with only a very small fraction of the cerium oxide. The possibility that the metals affect the

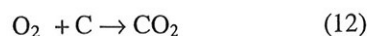
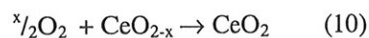


oxygen dynamics of the whole ceria phase itself is therefore not very likely. On the other hand it is much more possible that the metals enhance the activation of the reactants. Unpromoted cerium oxide showed very low activity for methane conversion. Methane must therefore be activated on the Pt or Rh surface. Activated methane (carbon or  $\text{CH}_x$  fragments) is not very likely to be mobile and spill over to the ceria surface. For the reduction of ceria to take place, there must be an exchange (transport) of oxygen to the metal surface where methane appears to react. Oxygen must migrate from the bulk of the cerium oxide to the surface of the promoter metal. Oxygen can be transported not only through bulk diffusion exchange between the two solids, but also through surface spillover [2]. It is probable that both these processes occur at the same time. Surface spillover would be most likely to occur when the surface is rich in oxygen. During multiple pulsing of methane over the material, the surface will be more and more depleted for oxygen and oxygen will be supplied by bulk diffusion from the crystal lattice of cerium oxide.

The unpromoted cerium oxide gave very low carbon formation. This indicates that reaction (6) is the rate-determining step when the promoters are not present. However, in presence of the promoters Pt and Rh, carbon formation is significant and the oxidation of carbon appears to be the rate-determining step. More carbon was deposited with Rh than with Pt as promoter. This indicates that coke gasification by oxygen transported from the cerium oxide to the noble metal surface is better with Pt than with Rh. The rate of methane activation with Rh could also be faster than with Pt. The latter would be in good accordance with the lower temperature of reduction with Rh than with Pt during  $\text{H}_2$ -TPR as shown in Figure 1.

*Regeneration with oxygen or carbon dioxide*

Large amounts of oxygen were taken out of the material during the reduction of cerium oxide by methane. It is also clear from Figure 3 and 4 that carbon deposition is significant during the methane pulsing. Carbon oxides were also formed when treating the used material with oxygen. Figure 5 shows what happened during multiple pulsing of oxygen or carbon dioxide over used materials from a treatment as shown in Figure 4. The regeneration process consisted both in removal of carbon from the surface of the material and recharging the bulk of the cerium oxide with oxygen. Both these processes require oxygen and they are therefore competitive what oxygen is concerned. It was suggested above that the promoters affected the activation of methane and that oxygen had to be transported to the metal surface by diffusion or spillover. The regeneration process in oxygen or carbon dioxide is not necessarily through the reverse oxygen transport as observed with methane, but can probably also occur directly with the ceria surface. Figure 5a shows the regeneration in oxygen at 700 °C. There was a simultaneous reoxidation of both the cerium oxide and carbon as in reactions (10-12).

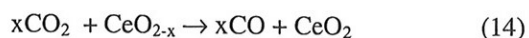
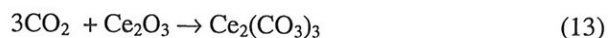


The yield of carbon monoxide per pulse of oxygen (Figure 5a) was fairly constant at only about 3 micromoles per 10 micromoles of oxygen injected. This shows that the oxidation of cerium oxide and carbon deposits occurred simultaneously. Only small amounts of carbon dioxide formed in the last pulse before the sample was completely oxidized and all the oxygen slipped through the reactor. Since the promoters enhance the activation of methane, carbon is most likely to be present on or near to the metal surface rather than the ceria surface. This was also strongly confirmed by the low formation of carbon on the

unpromoted  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  as shown in Figure 3a. The surface of the ceria phase must be much greater than the surface of the platinum or rhodium. It is therefore likely that the oxygen that adsorbed on ceria would go through reaction (10) and the oxygen that adsorbed on the metals would oxidize carbon in reactions (11) and (12).

The amount of the carbon oxides formed was used to estimate the total amount of carbon deposits after the treatment in methane. This will quantitatively be discussed below. The XRD pattern of a used and reoxidized sample at 700 °C was identical to the pattern of a fresh sample (Figure 2). Subsequent pulsing of methane after the regeneration in oxygen gave identical behavior as in Figure 4. The oxygen balance deduced from the oxygenated products in Figure 4 and the oxygen uptake in Figure 5 are in fairly good agreement (within 8%). It can therefore be concluded that after the reduction with methane, the regeneration with oxygen gave full recovery of the material. It is however interesting to note that the regeneration of the material yielded almost 100% carbon monoxide at the same time as the ceria was recovered. Carbon monoxide is much more applicable as a product from carbon removal than carbon dioxide.

The regeneration in carbon dioxide was studied both at 600 and 700 °C. The results are shown in Figure 5b and 5c. At both temperatures, the material balance of the first pulse showed that some kind of accumulation must have taken place. Carbonate formation is likely to occur on the cerium oxide surface [7,8,12]. Figure 5a and 5b indicate that reactions (13) and (14) occurred simultaneously. Thereafter, the carbon monoxide material balance indicated that carbon was also oxidized by carbon dioxide as in (15).



The carbon dioxide breakthrough occurred earlier during regeneration at 600 °C than at 700 °C indicating that high temperatures gave deeper oxidation of the material. The oxygen balance showed that at both temperatures, the reduced ceria had not been completely oxidized to CeO<sub>2</sub>. This was also confirmed by pulsing methane over the regenerated samples as shown in Figure 6. Treatment in oxygen after the reoxidation in carbon dioxide revealed that although some carbon had been removed according to reaction (15) the total did not correspond to all the amount of carbon deposited during the treatment in methane. After the regeneration with carbon dioxide at 600 °C and 700 °C the carbon removal (measured by subsequent pulsing of oxygen) was estimated to 58% and 74% respectively.

There were as mentioned some systematic discrepancies in the carbon and oxygen material balances when comparing the accumulation deducted from the sum of products during the pulsing of methane and carbon dioxide, and the actual carbon oxide formation measured from pulsing oxygen. These amounts were in general not equal and there was a clear general trend. The material balances from the pulsing of methane did always give more carbon than was measured afterwards with oxygen. The reactant pulsing over the material proceeded as follows: The gas pulse was injected and transported with helium over the material sample where it immediately reacted with oxygen in the material. The products that desorbed immediately were transported along with the helium further downstream to the packed column where they were separated and finally detected in the detectors. The helium flow through the system had to proceed for 12 minutes before all the products had come out of the column. It is also possible that there was a slow gasification of carbon deposits during the time in between the reactant pulses and the material was being flushed in helium. The discrepancies in the material balances all indicate that such a slow gasification took place.

Figure 3a shows that carbon was not formed on the unpromoted cerium oxide during pulsing with methane at 700°C. Figures 3b and 4 show that carbon was not formed on fully oxidized Rh and Pt promoted material (first pulse). During reduction with successive methane pulses significant amounts of carbon were indeed deposited on the promoted material. This result indicates that carbon is formed on the reduced noble metals.

Ruckenstein and Wang [13] pulsed a mixture of methane and oxygen in the ratio 2:1 over different catalyst samples. Successive pulsing over pure cerium oxide and over Rh promoted cerium oxide gave no carbon deposition at 750°C. Oxygen in the pulse seemed to prevent carbon deposition. During successive pulsing the conversion of methane decreased, while the selectivity to CO increased from zero up to a certain level. This is similar to the trend in our results where carbon was formed.

## Conclusion

The reaction between methane and cerium oxide to produce synthesis gas is strongly promoted by platinum and rhodium. The selectivity to synthesis gas depends on the degree of reduction of the cerium oxide. The reduction of  $\text{CeO}_2$  with methane was carried out until an estimated overall formula of  $\text{CeO}_{1.6}$ . This indicates a one step reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . During this reduction the conversion of methane decreased. The product ratios  $\text{H}_2/(\text{H}_2\text{O}+\text{H}_2)$  and  $\text{CO}/(\text{CO}_2+\text{CO})$  increased with increasing degree of reduction of the cerium oxide. The results indicate that carbon was formed on reduced Pt and Rh.

Regeneration of the used samples with oxygen gave complete removal of carbon as carbon monoxide with high selectivity. Simultaneously the reoxidation of cerium oxide became complete. Regeneration with carbon dioxide gave incomplete carbon removal and incomplete cerium oxide regeneration. During regeneration with carbon dioxide, the obtainable degree of oxidation increased with increasing temperature.

The present results suggest a highly selective route to synthesis gas from methane and oxygen in cyclic reaction with cerium oxide. In such a route, the cerium oxide acts as an intermediate oxygen carrier. The necessary temperature in such a process (~700 °C) is significantly lower than temperatures usually applied during conventional synthesis gas production (~900 °C).

#### Acknowledgment

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*Table 1: Composition and surface areas of the materials.*

<i>Sample</i>	<i>CeO<sub>2</sub></i>	<i>Pt</i>	<i>Rh</i>	<i>BET surface area</i>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-	-	-	198 m <sup>2</sup> /g
CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20 wt%	-	-	158 m <sup>2</sup> /g
Pt/CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20 wt%	0.5 wt%	-	159 m <sup>2</sup> /g
Rh/CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20 wt%	-	0.5 wt%	157 m <sup>2</sup> /g



**Figure captions:**

Figure 1: TPR analysis.

1A:  $\text{Ce}(\text{NO}_3)_2 + \gamma\text{-Al}_2\text{O}_3$  calcined in air at

a) 400 °C, b) 500 °C and c) 600 °C.

1B: a) 0.5 wt.% Pt/ $\gamma\text{-Al}_2\text{O}_3$ , b) 20 wt.%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , c) 0.25 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .

d) 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , e) 1.0 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .

1C: a) 0.5 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$ , b) 0.5 wt.% Rh/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .

Figure 2: X-Ray diffractograms of a) 20 wt.%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  calcined in air at 600 °C. b) 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , c) 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  reduced with methane and reoxidized in oxygen at 700 °C.

Figure 3: Methane pulsing (10 micromoles/pulse) over fresh samples (0.50 g) of a)  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  and b) 0.5 wt.% Rh/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  at 700 °C.

Figure 4: Methane pulsing (10 micromoles/pulse) over fresh a sample (0.50 g) of 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  at 700 °C.

Figure 5: Regeneration of 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  after treatments in methane as shown in Figure 5 with a) oxygen at 700 °C, b) carbon dioxide at 700 °C and c) carbon dioxide at 600 °C. All pulses of oxygen and carbon dioxide were 10 micromoles/pulse.

Figure 6: Methane conversion at 700 °C over regenerated 0.5 wt.% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .

a) Regenerated with  $\text{CO}_2$  at 700 °C, b) Regenerated with  $\text{CO}_2$  at 600 °C.

Figure 1

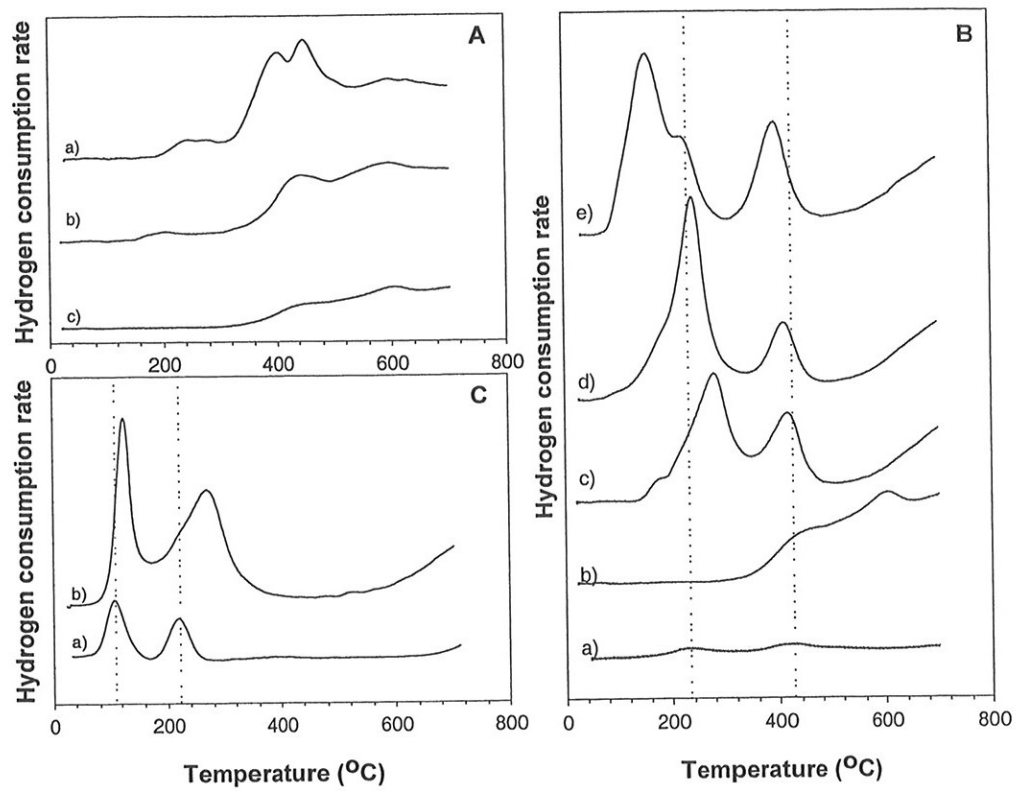


Figure 2

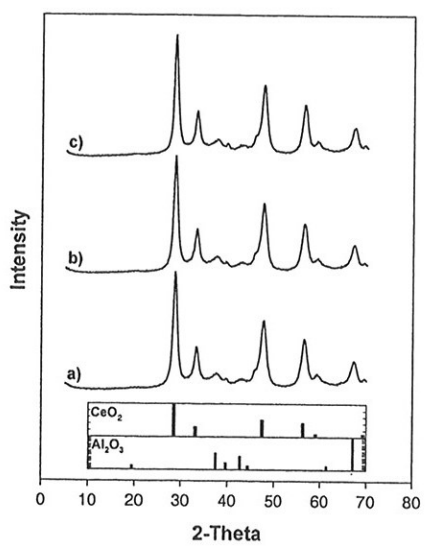


Figure 3

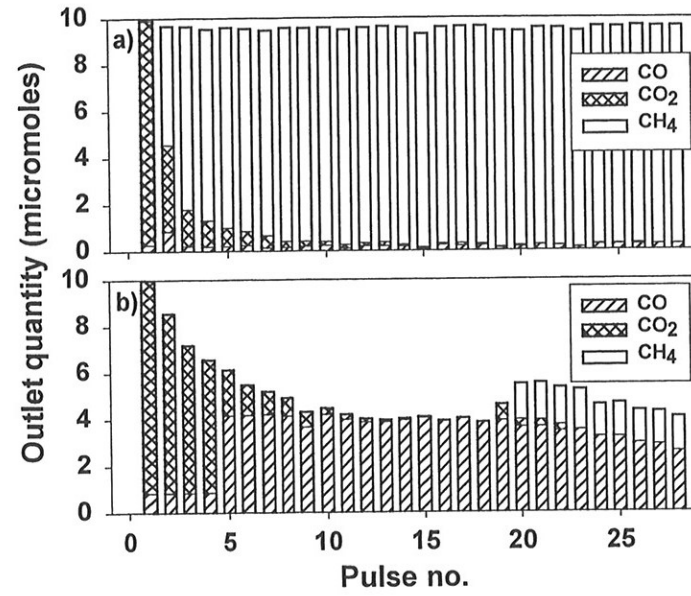


Figure 4

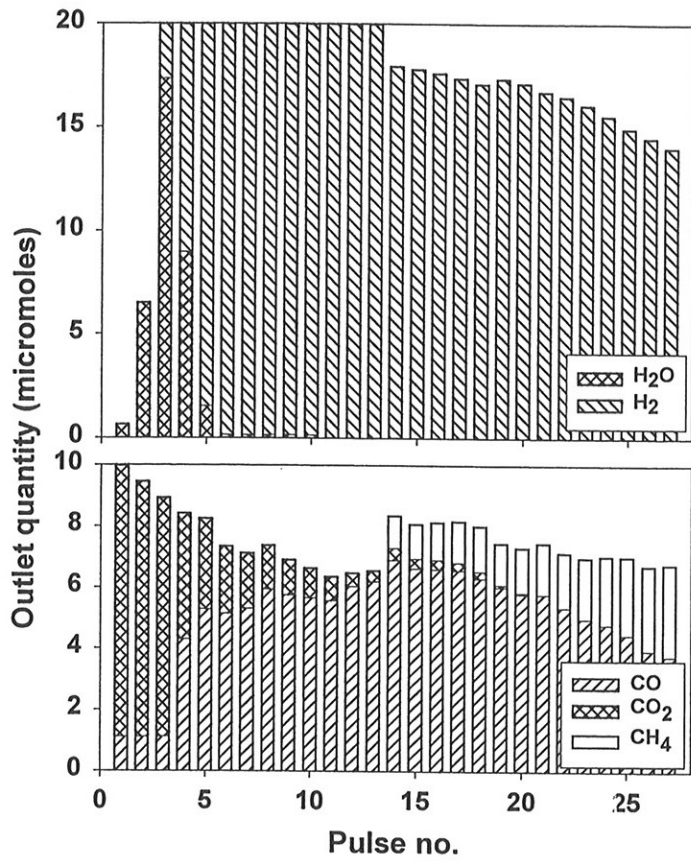


Figure 5

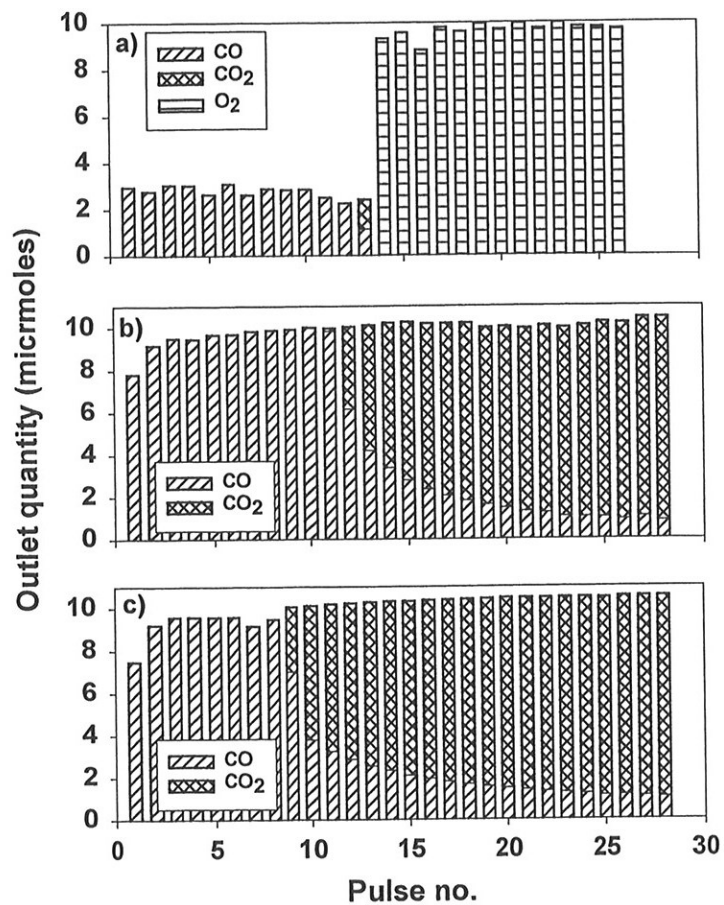
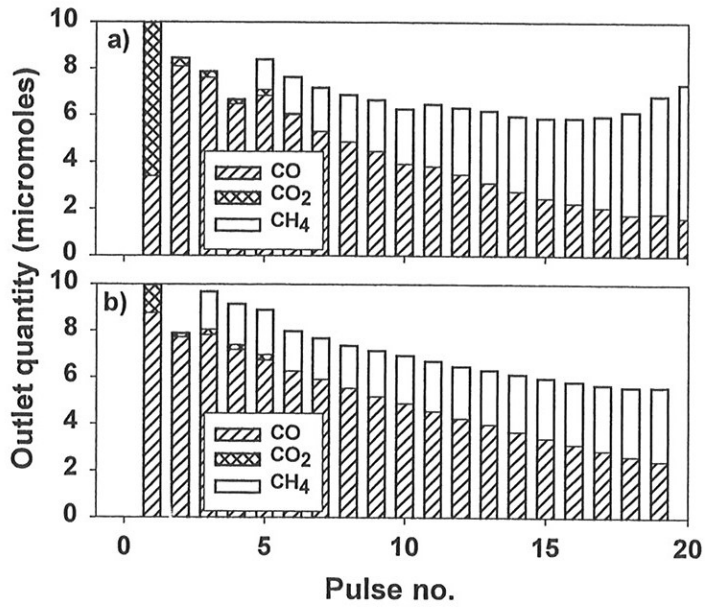


Figure 6







## Synthesis gas production from partial oxidation of methane with promoted cerium oxide by a cyclic gas-solid reaction

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### Introduction

Partial oxidation of methane to H<sub>2</sub> and CO has received much interest during the last years. At steady-state conditions where methane and oxygen are co-fed, the yield of synthesis gas from the direct oxidation is limited due to the consecutive formation of undesired products, i.e., carbon dioxide and water. An alternative approach is to carry out the partial oxidation anaerobically, i.e., without free oxygen in the gas phase.

This study deals with the formation of syngas from the reaction between methane and oxygen in cyclic operation where the oxygen is stored in Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Oxygen storage dynamics of cerium oxide is well described in the literature [1,2].

### Experimental

The experiments were carried out in a fixed-bed microreactor which has been described elsewhere [3]. The different flows were supplied by an automated 4-way valve allowing to switch abruptly from an oxidizing mixture (O<sub>2</sub>/Ar = 2.5/12.5 Nml,min<sup>-1</sup>) to a reducing one (CH<sub>4</sub>/He = 2.5/12.5 Nml,min<sup>-1</sup>) and vice-versa. The product gas at the reactor outlet was continuously analyzed by an on-line mass spectrometer (MS). The redox cycles were carried out at atmospheric pressure and at different temperatures (600 to 850°C) over 1 g of catalyst (τ = 4.2 s). Preparation and characterization of Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> have been described previously [4].

### Results and discussion

Fig. 1 reports on the product formation rates during the O<sub>2</sub>/Ar to CH<sub>4</sub>/He switch at 850°C. Initially, the reaction produces only carbon dioxide, followed by high quantities of water. When the CO<sub>2</sub> production drops, H<sub>2</sub> and CO appear rapidly and are slowly stabilized before finally decreasing when methane breaks through. The time with complete conversion of methane increases with increasing temperature from 0.5 min at 600°C to 3.0 min at 850°C. A separate experiment with switches from O<sub>2</sub> to inert to CH<sub>4</sub> as proposed by Pantu et al. [5], showed no different product formations than in the case of direct switches from O<sub>2</sub> to CH<sub>4</sub>. There seems therefore to be no effect of purging the system with inert and there is no significant contribution from methane and oxygen reacting directly without oxygen passing through the solid material. Carbon deposition on the material is significant during exposure to methane.

Fig. 2 shows the response of CH<sub>4</sub>, CO, CO<sub>2</sub> and O<sub>2</sub> for the CH<sub>4</sub>/He to O<sub>2</sub>/Ar switch. Carbon removal with 100% CO selectivity is obtained during the first 3 min with complete conversion of oxygen. A very limited quantity of CO<sub>2</sub> is produced just before the oxygen breakthrough. The reduced cerium oxide is reoxidized simultaneously with the carbon gasification.

According to the results presented in Figs. 1 and 2, it should be possible to produce synthesis gas with high selectivity even at low temperatures (< 850°C). The production of carbon dioxide and water occurs on the solid until a certain degree of reduction is reached, which is consistent with previous observations [5,6]. Control of the oxidation state of the

cerium oxide enables the production of CO<sub>2</sub> and H<sub>2</sub>O to be very limited at complete conversion of methane.

The product distribution during repeated cycles of methane (1 min) and oxygen (0.5 min) over Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> has also been studied. CO<sub>2</sub> and H<sub>2</sub>O are formed only when the material is fresh. After the second cycle, CO and H<sub>2</sub> are produced with very high selectivity.

The formation of CO as a function of time under methane exposure has been studied at different temperatures (600 to 850°C). No CO could be observed during the first 30 s but the formation of CO increases rapidly after about 30-50 s where the product from methane oxidation changes almost completely from CO<sub>2</sub> to CO. However, the formation of CO develops very differently depending on the temperature. At temperatures below 700°C there is an almost linear decrease, whereas for temperatures above 700°C the formation continues to increase until methane breakthrough.

The rate of formation of gaseous oxygenated products when most of the reactive surface oxygen has been removed, must be related to the rate of oxygen transport from the solid CeO<sub>2</sub> to the active Pt sites. Overall oxygen transport rates can be estimated from the rate of formation of oxygenated products (CO<sub>2</sub>, H<sub>2</sub>O, CO).

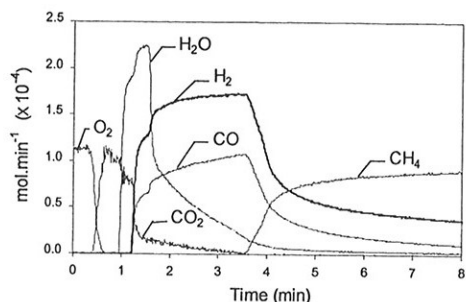


Fig. 1. Product formation rates during switching from O<sub>2</sub>/Ar to CH<sub>4</sub>/He at 850°C

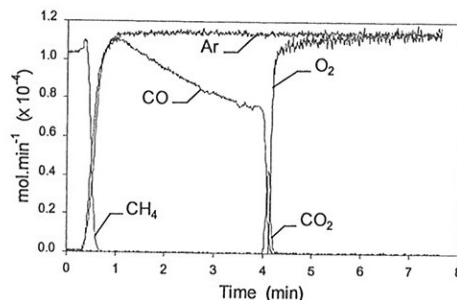


Fig. 2. Product formation rates during switching from CH<sub>4</sub>/He to O<sub>2</sub>/Ar at 800°C

## Conclusions

Higher yields of synthesis gas and higher conversion of methane can be achieved by operating the partial oxidation in redox cycles compared to steady-state operations. At anaerobic conditions, methane interacts with promoted CeO<sub>2</sub> and is partially oxidized to a H<sub>2</sub>/CO mixture and the reduced catalyst is regenerated and carbon deposits are gasified selectively to CO during the subsequent treatment with O<sub>2</sub>. Control of the oxidation state of the CeO<sub>2</sub> by adjustment of the redox cycles time allows to limit the formation of H<sub>2</sub>O and CO<sub>2</sub> at complete conversion of methane. Moreover, step transient operation allows to avoid safety problems of the O<sub>2</sub>/CH<sub>4</sub> mixture. Oxygen transport in the solid CeO<sub>2</sub> appears to be rate determining for the formation of gaseous products.

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