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# Partial oxidation of propane using micro structured reactors

Helmut Pennemann*, Volker Hessel, Gunther Kolb, Holger Löwe, Ralf Zapf

*Institut für Mikrotechnik Mainz GmbH, Carl-Zeiss-Straße 18-20, 55129 Mainz, Germany*

## Abstract

Various catalysts based on rhodium, palladium and platinum on γ-alumina were wash-coated into micro structured reactors. The catalysts were applied in the partial oxidation of propane aiming for synthesis gas. Best results were achieved with pure rhodium and bimetallic rhodium/platinum catalysts having at least a rhodium concentration exceeding 0.5 wt.%. With rhodium-based catalysts complete propane conversion was observed. Selectivities of hydrogen and carbon monoxide were close to the thermodynamic equilibrium. During long-term operation, coke formation was observed resulting in an increase of the pressure drop over the reactors. Upon inspection of the reactors it turned out that the micro channels were marginally covered with coke depositions but the outlet tube of the reactor was found to be fully plugged. With the help of a simulated reformate it was found that coke formation was only little dependent on the operating temperature. In contrast, coke formation was significantly reduced by the employment of reaction plates made of a nickel-free stainless steel and by a protective coating consisting of α-alumina.

*Keywords:* Micro structured reactor; Wash-coat; Partial oxidation; Propane; Hydrogen production; Coke formation; Protective coating

## 1. Introduction

Beyond its industrial utilisation, hydrogen aroused special interest as an environmentally friendly fuel for fuel cells and combustion engines within the last decades [1,2]. Prior to the introduction of hydrogen as energy carrier for the mass markets, requirements concerning the hydrogen supply have to be addressed. Depending on the application, hydrogen can either be generated on-site or provided in storage tanks using liquefaction, gas compression, or other storage technologies [3–6]. The on-site production of hydrogen requires the development of cost-effective technologies addressing hydrogen efficiency, system size, weight, start-up time, and life time which is affected by temperature cycles and catalyst deactivation.

Typically, hydrogen production is carried out by steam reforming, autothermal reforming, or partial oxidation [7]. The partial oxidation of light hydrocarbons, among others propane and mixtures of propane and butane (LPG), is particularly advantageous when system compactness is the main target. Firstly, these gases are readily available and a distribution grid does already exist. In addition, they can be distributed safely and cost-efficiently as liquids under moderate pressure. Secondly, hydrogen formation is normally observed at contact times in the lower ms-range allowing high throughputs and small reactor dimensions, respectively. In turn, small reactor dimensions and weight are also beneficial for a low start-up time demand. Additionally, the partial oxidation is exothermal. Thus, external heating is not required during continuous operation resulting in a more compact design of the system.

Due to the high heat release, an integrated reactor/heat exchanger design appears to be beneficial to avoid high reaction temperatures which significantly affect the life time of most catalysts. For such an integrated design micro structured reactors can be employed [8,9]. The high specific surface area improves the heat removal capabilities which smooth out the typical hot spot of the partial oxidation.

High throughputs in small reactors also require highly efficient catalysts. This specification is particularly met by catalysts based on noble metals, such as rhodium, palladium, and platinum. In the past, these metals were impregnated on oxide supports and then investigated in foam monoliths. At contact times of a few milliseconds and oxygen/propane ratios in the range of 1.5–2, the highest propane conversions and hydrogen selectivities were observed with rhodium. In comparison, platinum and palladium are characterised by the formation of considerable amounts of ethylene and coke, respectively [10,11].

Blank activity tests indicating thermal ignition of the reactants at furnace temperatures above 650 °C demonstrated the presence of homogeneous reactions in such alumina foams [12]. At 850 °C even complete conversion was achieved with

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* Corresponding author. Tel.: +49 6131 990425; fax: +49 6131 990205.
*E-mail address:* pennemann@imm-mainz.de (H. Pennemann).

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a non-impregnated alumina foam. Determination of temperature profiles inside a rhodium impregnated foam confirmed a hot spot and its axial position was related to the furnace temperature. Tests performed for a duration of 9 h at 700 °C indicated a sufficient long-term stability of the rhodium catalyst applied [12].

Besides noble metal catalysts, the propane oxidation was also investigated over nickel-based catalysts in small fixed bed reactors [13,14]. It was reported that the extent of carbon formation can be decreased in the presence of alkali metal and rare earth oxides reducing the Lewis acidity of the catalyst [14].

Experiments in an annular reactor at temperatures below 700 °C revealed the presence of different routes for the formation of hydrogen and carbon monoxide [15]. In the case of platinum on $\gamma$-alumina, a direct oxidation reaction was assumed to lead to synthesis gas. In contrast, over rhodium on $\alpha$-alumina, the presence of both, direct oxidation and secondary reactions, such as steam or $CO_2$ reforming, were assumed to be the relevant reactions.

Recently, the partial oxidation of propane was also investigated applying metallic monoliths consisting of a stack of micro structured platelets coated with a rhodium catalyst [16]. Similar to former mentioned alumina foams, temperature profiles were determined along the micro channels. Due to the more efficient heat transfer along the micro channels in the metallic monolith, the temperature rise was much lower compared to alumina foams.

In the present contribution, sandwich-type reactors were employed to investigate rhodium-, platinum-, and palladium-based catalysts in the partial oxidation of propane aiming for synthesis gas. First results were published elsewhere [17]. The catalysts were deposited as a thin film onto the surface of the micro channels using a wash-coating/impregnation procedure [18]. Since coke formation was observed in long-term experiments, inertness of various materials and coatings were investigated by blank activity experiments.

## 2. Experimental

### 2.1. Reactor and experimental set-up

All experiments were carried out with sandwich-type reactors composed of two platelets each having 14 channels with 500 μm width and 250 μm depth. The micro channels were made by wet-chemical etching using an aqueous iron chloride solution. After passivation layers and catalysts had been coated into the micro channels, the sandwich-type reactors were sealed by laser welding. For catalyst screening the micro reactors were placed into a metal block equipped with a heating cartridge. The feed gases, propane, synthetic air and nitrogen as a flush gas, were supplied by mass flow controllers. The reactor configurations used within this study are summarised in Table 1.

### 2.2. Investigation of blank activity and coke formation

The blank activity of the reactor material was investigated with the sandwich-type reactors at a total flow rate of 100 ml min$^{-1}$, an O/C ratio of 1 and temperatures in the range of 700 to 850 °C. According to Table 1, two reactor configurations were used for the blank activity tests having either micro channels with a $\gamma$-$Al_2O_3$-coating (reactor configuration 1) or uncoated micro channels (reactor configuration 2).

Coke formation was also investigated with sandwich-type reactors being either uncoated (reactor configurations 2 and 3) or having an $\alpha$-alumina coating (reactor configuration 4). At the beginning of each experiment, the reactor was pre-treated with a continuous hydrogen flow of 20 N ml min$^{-1}$ at 700 °C for 1 h. Subsequently, the furnace temperature was adjusted to either 650 °C or 700 °C. For the coke formation experiments a simulated reformate containing 73.7 vol.% hydrogen, 13.8 vol.% carbon dioxide, and 12.5 vol.% carbon monoxide was fed into the reactor using a flow rate of 100 N ml min$^{-1}$. The composition of the reactor effluent gas was determined every 20 min using the same GC as described in Section 2.3. The experiments were terminated when an increase of the pressure drop indicated a plugging of the reactor by coke formation.

### 2.3. Catalyst preparation

The catalysts were introduced into the micro channels prior to laser welding by a sequential procedure comprising wash-coating, drying, calcination, impregnation, and second calcination. As catalyst support $\gamma$-$Al_2O_3$ (Alfa Aesar) was used having a specific surface of 80 m$^2$ g$^{-1}$. The suspended support material was introduced into the micro channels by a fill-in wipe-off technique followed by a drying and a calcination step at 600 °C [18]. Subsequently, the support was impregnated with the respective metal salt solutions and calcined a second time at 450 °C. Table 2 provides an overview of the samples prepared.

Table 1
Reactor configuration used for the investigation of the blank activity, coke formation and catalyst screening

| No. | Reactor configuration | Application area |
|---|---|---|
| 1 | Reaction plates: Ni-containing stainless steel (1.4841), coating of the micro channel structure either with $\gamma$-alumina (for blank activity test) or with a catalyst wash-coat (for catalyst screening) | Blank activity tests and catalyst screening |
| 2 | Reaction plates: Ni-containing stainless steel (1.4841); no coating inside the reactor | Blank activity tests and coke formation |
| 3 | Reaction plates: Ni-free stainless steel (1.4742); no coating inside the reactor | Investigation of coke formation |
| 4 | Reaction plates: Ni-containing stainless steel (1.4841); internal of reactor is entirely coated with $\alpha$-alumina | Investigation of coke formation |

Table 2
Catalysts prepared for the partial oxidation

| No. | Metal | Concentration [wt.%] | Support |
|---|---|---|---|
| 1 | Rh | 1 | $\gamma$-$Al_2O_3$ |
| 2 | Pt | 1 | $\gamma$-$Al_2O_3$ |
| 3 | Pd | 1 | $\gamma$-$Al_2O_3$ |
| 4 | Pt | 2 | $\gamma$-$Al_2O_3$ |
| 5 | Rh/Pt | 0.1/1.9 | $\gamma$-$Al_2O_3$ |
| 6 | Rh/Pt | 0.5/1.5 | $\gamma$-$Al_2O_3$ |
| 7 | Rh/Pt | 1/1 | $\gamma$-$Al_2O_3$ |
| 8 | Rh/Pt | 1.5/0.5 | $\gamma$-$Al_2O_3$ |
| 9 | Rh/Pt | 1.9/0.1 | $\gamma$-$Al_2O_3$ |
| 10 | Rh | 2 | $\gamma$-$Al_2O_3$ |
| 11 | Rh/Pt | 1/1 | $\gamma$-$Al_2O_3$, MgO |

### 2.4. *Procedure for partial oxidation of propane*

At the beginning of each experimental run, the freshly prepared catalyst was reduced at 700 °C at a hydrogen flow rate of 20 N ml $min^{-1}$ for 1 h. Without further pre-treatment the partial oxidation was initiated at 700 °C. After a sample had been taken on-line for analysis the reactor temperature was increased by 10 °C. This procedure was repeated until a final temperature of 850 °C was reached. Subsequently, long-term stability of the catalyst was investigated typically at 750 °C. Experiments were carried out at O/C-ratios in the range of 1.0–1.3. Flow rates were adjusted to a total flow rate of 400 N ml $min^{-1}$ with respect to the reactants, resulting in a GHSV of 274,000 $h^{-1}$, in a WHSV ranging from 1440 to 1770 l $h^{-1}$ $g_{catalyst}{}^{-1}$ and an overall pressure drop of approximately 0.8 bar.

Product gases were analysed by an on-line gas chromatograph (Trace GC, Thermo-Finnigan). The two-channel GC was equipped with a pre-column Porapak N, a Haysep Q column, a molecular sieve 5A column and a combined Haysep and mol sieve column. Both channels were equipped with thermal conductivity detectors.

## 3. Results and discussion

### 3.1. *Blank activity experiments and investigation of coke formation*

Previous to the catalyst screening experiments it was verified by blank activity tests that the reactor material and the oxide support do not have a dominating catalytic activity. These experiments were performed at a total flow rate of 100 ml $min^{-1}$, an O/C ratio of 1 and temperatures in the range of 700–850 °C. Two reactors were used having either micro channels with a $\gamma$-$Al_2O_3$-coating or uncoated micro channels.

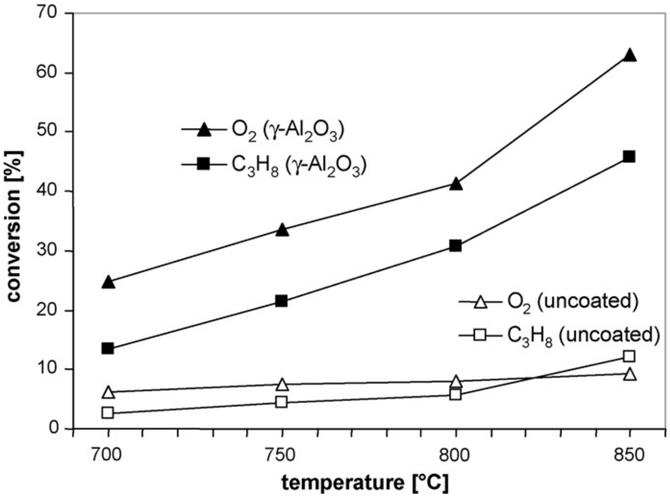

Fig. 1. Blank activity tests of reactor material and oxide support using reactants (O/C: 1).

In the case of the uncoated micro channels, propane and oxygen conversions of up to 12% and 10%, respectively, were found (Fig. 1). In comparison, the $\gamma$-alumina coating resulted in a much higher blank activity. Conversions up to 46% for propane and up to 63% for oxygen were determined. In both cases, relatively high selectivities towards propylene and ethylene were observed.

In general, the $\gamma$-alumina seems to promote the propane conversion much more than the uncoated stainless steel surface of the reactor housing. Additionally, during screening the largest part of the internal reactor surface is covered with a catalyst having a $\gamma$-alumina support which significantly decreases the remaining surface area of uncoated stainless steel. Hence, it is concluded that the blank activity of the reactor housing with regard to the conversion of propane can be neglected.

At first glance, the results of the blank activity tests appeared to be contradictory to the coke formation observed in the experiments reported in Sections 3.4–3.6. But a more detailed inspection showed that coke formation was only found when full propane conversion and high selectivities for hydrogen and carbon monoxide were achieved. Furthermore, coke formation occurred particularly in the reactor outlet tube. Consequently, it was assumed that coke was formed by a downstream reaction such as the carbon monoxide reduction by hydrogen.

This assumption was verified experimentally by investigating the coke formation in uncoated reactors. Instead of propane and air, the reactor was fed with a simulated reformate containing

Table 3
Catalytic activity of an uncoated reactor at 650 and 700 °C using a simulated reformate (GC concentrations in vol.%)

| Time (h)/comments | Reactor configuration 2 temperature: 700 °C | | | | Reactor configuration 2 temperature: 650 °C | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $H_2O$ | CO | $CO_2$ | $H_2$ | $H_2O$ | CO | $CO_2$ |
| 0/feed composition | 73.0 | 0 | 12.9 | 14.1 | 73.0 | 0 | 12.9 | 14.1 |
| 0.4/1st analysis | 70.2 | 2.8 | 15.4 | 11.5 | 70.6 | 2.5 | 12.3 | 14.5 |
| 6.0/clogging at 700 °C | 66.1 | 7.3 | 18.2 | 8.2 | 67.6 | 6.1 | 17.5 | 9.0 |
| 7.4/clogging at 650 °C | – | – | – | – | 65.9 | 7.5 | 18.6 | 7.9 |

Table 4
Catalytic activity of an reactor made of nickel-free stainless steel (reactor configuration 3) and an α-alumina coated reactor (reactor configuration 4) at 700 °C using a simulated reformate (GC concentrations in vol.%)

| Time (h)/comments | Reactor configuration 3 nickel-free stainless steel | | | | Reactor configuration 4 α-alumina coating | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $H_2O$ | CO | $CO_2$ | $H_2$ | $H_2O$ | CO | $CO_2$ |
| 0/feed composition | 73.0 | 0 | 12.9 | 14.1 | 73.0 | 0 | 12.9 | 14.1 |
| 0.4/1st analysis | 72.0 | 2.3 | 13.8 | 11.8 | 71.5 | 1.6 | 13.4 | 13.3 |
| 6.0 | 70.1 | 4.4 | 15.2 | 10.2 | 71.9 | 1.3 | 13.2 | 13.6 |
| 7.4 | 70.1 | 4.4 | 15.4 | 10.0 | 71.9 | 1.2 | 13.2 | 13.6 |
| 12.7/clogging of reactor 3 | 69.0 | 5.6 | 16.3 | 9.1 | 72.0 | 1.2 | 13.1 | 13.7 |
| 55/clogging of reactor 4 | | | | | 69.4 | 4.0 | 14.5 | 11.7 |

hydrogen, carbon dioxide, and carbon monoxide. The conversion at reactor temperatures of 650 and 700 °C was determined by online GC analysis as described above.

As summarised in Table 3 the furnace temperature had only a marginal effect on coke formation. When the temperature was decreased from 700 to 650 °C time period was shifted by 1.5 h only until a significant increase of the pressure drop was observed. At both temperatures there was a slight change in the composition of the simulated reformate feed. Compared to the original composition, carbon dioxide and hydrogen were consumed whereas carbon monoxide and water were formed. Methane formation was not observed until the pressure drop increased significantly owing to the plugging of the reactor.

The observed conversion may be explained by the reverse water gas shift reaction resulting in the formation of carbon monoxide and water. It was presumed that carbon monoxide was then partly reduced by hydrogen yielding in coke formation. A minor carbon formation is also in accordance with the material balance of the carbon species indicating that on average about 0.7% of the carbon was accumulated in the reactor.

The formation of coke is known as a complex phenomenon, since it is particularly affected by the chemical composition of the steel or alloy surface, respectively. Nickel and iron typically show higher activity towards coke deposition than chromium [20]. Additionally, chromium promotes passivation due to the formation of a chromia layer [21]. To assess the impact of nickel on coke formation, the experiment described above was repeated with a reactor made of a nickel-free stainless steel (Table 4). Compared to the reactor made of a nickel-containing stainless steel, the increase of pressure drop was retarded by about 6 h.

Subsequently to the termination of the experiments illustrated in Tables 3 and 4, the reactors were cut open to inspect the extent of coke formation and to identify the reactor parts responsible for the increase of the pressure drop. Images of the micro channel structure after the experiments are shown in Fig. 2. In the case of the reactor made of a nickel-containing stainless steel (left) all micro channels are covered completely with coke. In contrast, coke formation was significantly reduced in the case of the nickel-free stainless steel (Fig. 2, right). The surface of the micro channels was covered only with a thin coke layer.

A large amount of coke was found in the inlet and outlet tubes of both reactors. The tubes were totally plugged which turned out to be original reason of the pressure drop increase. This suggests that coke did not originate from gas phase reactions but is formed primarily by the catalytically active surface of the nickel-containing stainless steel in the reactor inlet and outlet tubes.

### 3.2. Passivation of the stainless steel surface

Besides the employment of a nickel-free stainless steel, the effect of a protective coating on the coke formation was investi-

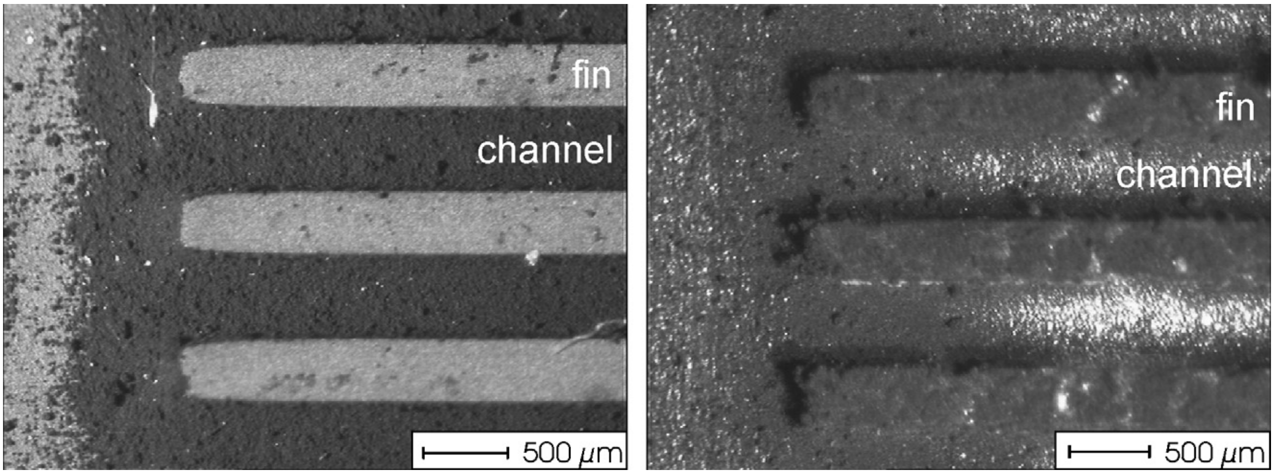

Fig. 2. Coke deposits in micro channels of uncoated reactors made of a nickel-containing steel after 6.5 h (left, corresponds to Table 3) and made of a nickel-free steel after 12.5 h (right, corresponds to Table 4).

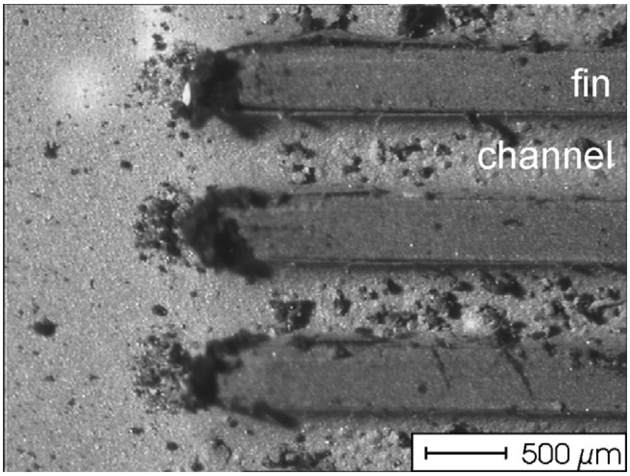

Fig. 3. Coke deposits in the micro channels of an α-alumina-coated reactor at 700 °C after 55 h (flow direction: from the left to the right; corresponds to Table 4).

gated. For these experiments, the reaction plates and connecting tubes were manufactured from a nickel containing stainless steel and subsequently coated with a protective layer. The effect of the protective layer was investigated applying the simulated reformate according to the procedure described above.

The results obtained for the α-alumina coating are shown in Table 4. Compared to the uncoated reactor (Table 3), plugging of the reactor was retarded by about 50 h. Furthermore, the gas compositions flowing through the reactor remained nearly unchanged indicating also a low catalytic activity with regard to the reverse water gas shift reaction.

Again the reactor was cut open after termination of the experiment. Compared to the uncoated reactor (Fig. 2, left), the α-alumina coating decreased significantly the coke deposition (Fig. 3). Only little coke was found in front of the fins and in the micro channels.

A larger amount of coke was found in the reactor at positions which are difficult to coat entirely with α-alumina. This is particularly true for the borehole where the inlet and outlet tube is inserted. Nevertheless, most of the coke was found again in the inlet and outlet tube of the reactor.

Based on these results it may be concluded that coke formation can only be reduced by the α-alumina coating but not totally prevented. Since the increase of the pressure drop resulted again from a plugging in the inlet and outlet tube, coke formation may be ascribed to the catalytic activity of the stainless steel surface.

### 3.3. Catalytic activity of pure transitions metals

In the first series of experiments, catalysts containing a single transition metal such as rhodium, platinum, and palladium on alumina were investigated with regard to conversion and selectivity (Figs. 4–6). In the case of a catalyst loading of 1 wt.%, conversions over platinum and palladium catalysts did not exceed 43%. This can be explained by the high selectivity of platinum and palladium towards total oxidation [19]. Hence,

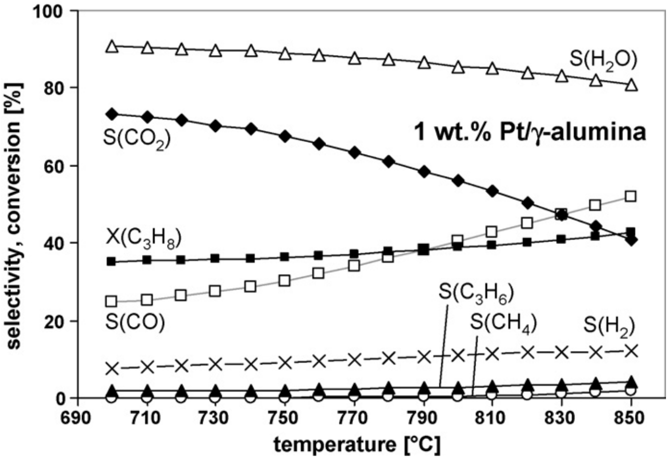

Fig. 4. Conversions and selectivities over fresh platinum catalyst at different temperatures (O/C: 1, total flow rate: 400 ml $\text{min}^{-1}$).

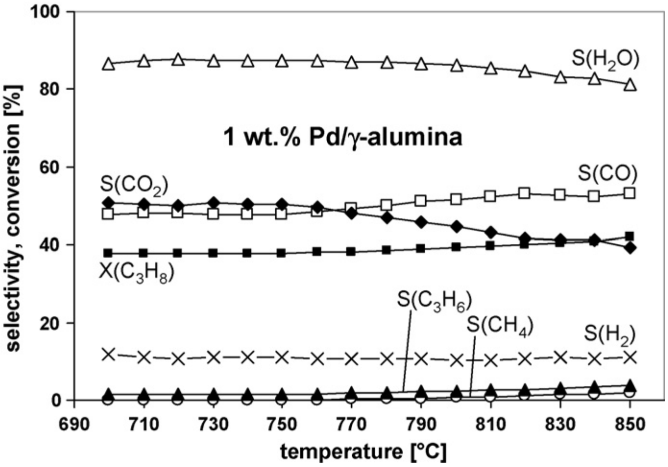

Fig. 5. Conversions and selectivities over fresh palladium catalyst at different temperatures (O/C: 1, total flow rate: 400 ml $\text{min}^{-1}$).

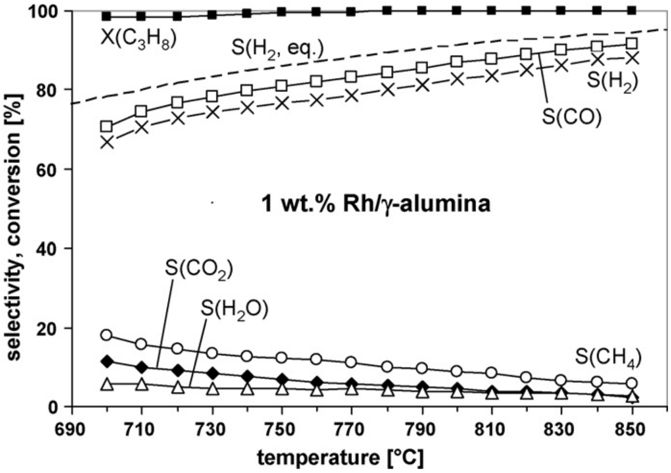

Fig. 6. Conversions and selectivities over fresh rhodium catalyst at different temperatures (O/C: 1, total flow rate: 400 ml $\text{min}^{-1}$).

oxygen is entirely consumed and large amounts of water and carbon dioxide were found (Figs. 4 and 5). Correspondingly, the hydrogen selectivities were rather low. This poor performance was only slightly improved by increasing the reaction temperature up to 850 °C.

In comparison, propane conversion up to 100% was achieved over the rhodium catalyst having a metal loading of 1 wt.% (Fig. 6). Similar to the platinum and palladium catalysts, oxygen is completely consumed but in contrast a lower selectivity towards water and carbon dioxide was found which even further decreased with increasing reaction temperature. Moreover, significantly higher selectivity towards hydrogen and carbon monoxide was determined.

Since rhodium is typically used as a catalyst for steam reforming and carbon dioxide reforming, the observed selectivities can be explained by excellent reforming capabilities which are complemented by adequate oxidation capabilities. In fact, two reaction paths are under discussion in literature: Firstly, a direct scheme assuming that a propane molecule is partially oxidised resulting straightforward in hydrogen and carbon monoxide and secondly, a two-step scheme comprising an oxidation step which is followed by reforming reactions. In the case of the partial oxidation of propane over rhodium catalysts, the dominance of the two-step scheme is reported in literature [15].

This is in accordance with the temperature dependence of the selectivities which was observed here for the rhodium catalyst (Fig. 6). The selectivity towards the main products, namely hydrogen and carbon monoxide, increased at higher reaction temperature while a reduced selectivity towards the oxygen sources, water and carbon dioxide, was observed. The hydrogen selectivities determined experimentally were close to the hydrogen selectivities calculated from the thermodynamic equilibrium.

In the case of platinum and palladium containing catalysts, formation of by-products, such as propylene, ethylene, and methane, was observed which slightly increase with rising temperature. In comparison, only methane was found during the investigation of the rhodium catalyst. At an O/C ratio of 1 the selectivities towards methane decreased from 18% to 6% when increasing the reaction temperature from 700 to 850 °C.

### 3.4. Deactivation of pure and bimetallic catalysts

After investigating the catalytic activity at different temperatures, deactivation of the catalyst was checked at 750 °C. The propane conversion observed is summarised in Fig. 7.

No significant deactivation was found for the catalysts based on platinum and palladium at loadings of 1%. Propane conversion after 15 h test duration remained stable compared to the initial conversion. In contrast, the experiment with the pure rhodium catalyst had to be terminated after 8 h because the pressure drop over the reactor exceeded 1 bar. Since coke formation was assumed to be the reason for the increase of the pressure drop, the micro structured reactor was cut open. Interestingly, no coke deposits were found in gas distribution zone at the reactor inlet and in the channels coated with the catalyst whereas minor coke deposits were found at the reactor outlet. However, the amount of coke inside the reactor was too low to explain the increasing pressure drop. Finally, it was determined that the rise in pressure originated from a small coke plug formed inside the outlet tube of the reactor.

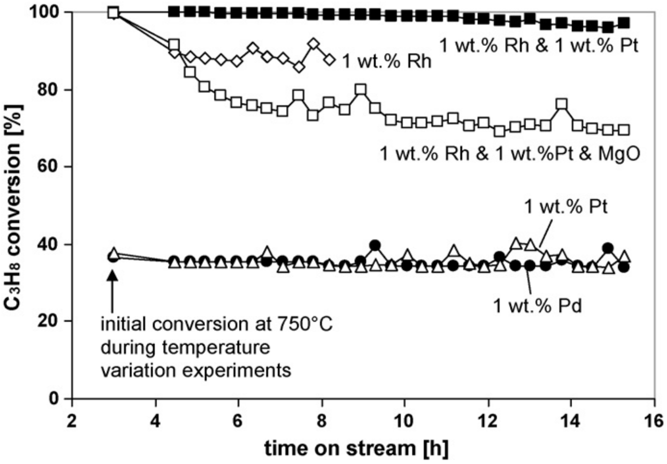

Fig. 7. Conversions over fresh catalysts at 750 °C (O/C: 1, total flow rate: 400 ml $\min^{-1}$).

Subsequently, the rhodium catalyst was modified by a co-impregnation of γ-alumina with 1 wt.% rhodium and 1 wt.% platinum. As depicted in Fig. 7, deactivation of the bimetallic catalyst was slowed down compared to the pure rhodium catalyst. Only a slight drop of the propane conversion was observed after 11 h. The increased conversion compared to the pure rhodium catalyst can be explained by both the increased catalyst loading and a beneficial effect of platinum on the course of the reaction. At least, there is a small effect on the reaction pathways, which is indicated by slightly higher selectivities of the oxidation products such as water and carbon dioxide. But a correlation of the change in selectivity and decelerated deactivation needs further investigations.

In a further experiment, magnesia was added to the bimetallic catalyst with the intention to improve the resistance of the oxide support with regard to sintering. However, the addition of magnesia resulted in a higher decrease of the propane conversion.

### 3.5. Effect of different O/C ratios

To reduce coke formation observed during the experiment over the pure rhodium catalyst (Fig. 7), the O/C ratio was increased from the stoichiometric ratio (1.0) up to 1.3. For each O/C ratio a fresh catalyst with 1 wt.% rhodium on γ-alumina was used. In the initial experiments oxygen was entirely consumed and propane conversion was in the range from 95 to 100%. The corresponding selectivities of hydrogen and methane are summarised in Fig. 8. Starting from an O/C ratio of 1.0 it is obvious that methane selectivities were decreased at higher O/C ratios. Moreover, hydrogen selectivities were improved in particular at temperatures below 800 °C. Above this temperature, similar hydrogen selectivities were determined for O/C ratios from 1.0 to 1.2 but higher O/C ratios resulted in a decrease of the hydrogen selectivity. Since the methane concentration was quite low at an O/C ratio of 1.3, hydrogen might be consumed by the excess

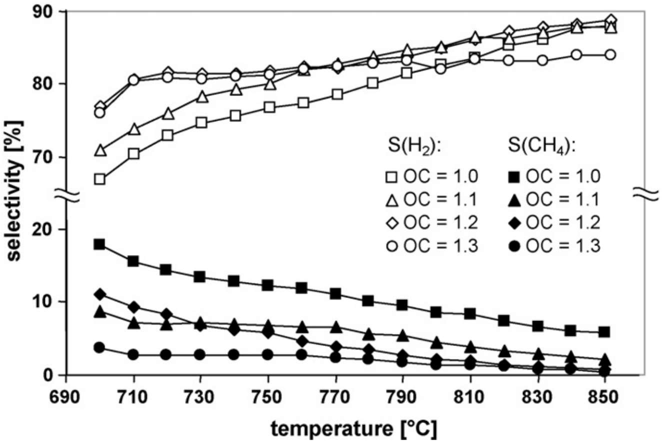

Fig. 8. Hydrogen and methane selectivities over rhodium (1 wt.%) on γ-alumina catalysts at different temperatures and O/C ratios (total flow rate: 400 ml min$^{-1}$).

oxygen present resulting also in higher selectivities of water (not shown in the graph).

After each of the experiments discussed above, catalyst performance with respect to deactivation was investigated at 750 °C without any further treatment of the catalysts. It was found that O/C ratios of 1.1 and 1.2 did not affect the coke formation, since an increase of the pressure drop was found after 7–8 h. Only at an O/C ratio of 1.3 operating time was nearly doubled.

### 3.6. *Catalytic activity of bimetallic rhodium/platinum catalysts*

Based on the good results with the mixed rhodium/platinum catalyst (Fig. 7) and the improved hydrogen selectivities at increased O/C ratios (Fig. 8), further experiments were carried out with bimetallic catalysts at an O/C ratio of 1.2. All applied bimetallic catalysts had the same overall metal loading of 2 wt.% but varying rhodium/platinum ratios were investigated. The selectivities summarised in Fig. 9 were achieved at a furnace temperature of 800 °C. In the case of the pure platinum catalyst propane conversion was at 43% and water and carbon dioxide were determined as the products with the highest selectivities. A small amount of rhodium was sufficient to cause a change of the selectivity towards hydrogen and carbon monoxide. At rhodium loadings higher than 0.5%, propane was completely consumed and hydrogen selectivities of up to 85% were achieved.

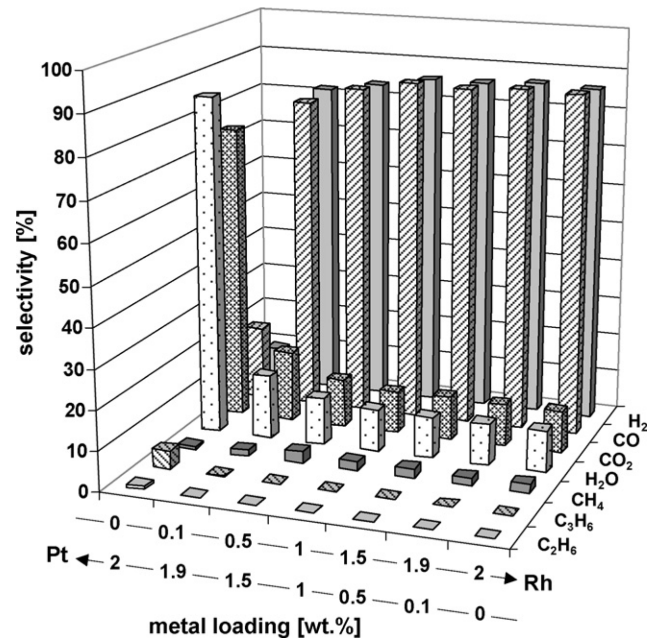

Fig. 9. Selectivities of bimetallic rhodium/platinum catalyst (total metal loading: 2 wt.%; furnace temperature: 800 °C, O/C: 1.2, total flow rate: 400 ml min$^{-1}$).

Again stability of the catalyst with respect to time was investigated at 750 °C after each experiment. In the case of rhodium loadings of 0 to 0.5 wt.% pressure drop in the reactor was found to be constant during an operating time of 18 h.

Although higher rhodium loadings of 1–2 wt.% resulted in complete propane conversion, all experiments were terminated after 8–14 h due to an increase of the pressure drop. By opening of the reactors it was proven that coke formation in the reactor outlet tube was the primary reason.

## 4. Summary and outlook

Various catalysts based on rhodium, platinum, palladium and mixtures of rhodium and platinum were prepared and tested in the partial oxidation of propane. Since oxygen was entirely consumed in every experiment, high oxidation capabilities can be assigned to all catalysts tested. Propane conversion was strongly dependent on the catalyst. In case the of rhodium, complete conversion and high selectivities towards hydrogen and carbon monoxide close to thermodynamic equilibrium were achieved. In contrast, over platinum and palladium products of total oxidation, such as water and carbon dioxide, were favoured. Homogeneous reactions were found to play a minor role when the oxide support was impregnated with catalyst. Only in the case of platinum and palladium small traces of ethylene and propylene were detected. In comparison, no products of homogeneous reactions were observed over rhodium-based catalysts. Furthermore, bimetallic rhodium/platinum catalysts were investigated and turned out to be as selective as a pure rhodium catalyst when the rhodium concentration of the bimetallic catalysts was higher than 0.5 wt.%.

In general, it was determined that in the case of complete or nearly complete propane conversion, the experiment had to be terminated after a certain time due to an increase of the pressure drop. By opening of the reactor coke formation was found to be the cause of the plugging. Although both reactor parts, the reaction plates and the connection tubes, were made of a nickel-containing stainless steel, coke formation in the reactor outlet tube was the crucial factor. This was experimentally confirmed by means of a simulated reformate containing hydrogen, carbon dioxide and carbon monoxide.

Further tests indicated that coke formation may be reduced at a higher O/C ratio of 1.3. Unfortunately, a further addition of air is also accompanied by a dilution of the hydrogen by nitrogen. In turn, this would reduce the efficiency of the fuel cell with regard to the exploitation of hydrogen. As an alternative to increasing the O/C ratio, the catalytically active stainless steel surfaces may be passivated by a protective coating. The application of a protective coating in micro structured reactors was already demonstrated for other selective oxidations [22] and is also an important topic for petrochemical reactors [23]. In a first experiment the stainless steel surface of the reaction plates and the connecting tubes were coated with α-alumina. In preliminary experiments with the simulated reformate, coke formation was retarded by about 50 h compared to the uncoated reactor.

Reducing coke formation is a critical task for future investigations since the integrated reactor/heat exchanger for the partial oxidation of propane requires runtimes of at least 1000 h. For this reason, further protective coatings will be investigated. A second focus will be the evaluation of other steels or alloys which are not catalytically active with regard to coke formation. This is important for both, further screening experiments addressing the long-term stability of the catalysts and the selection of an appropriate construction material for an integrated reactor/heat exchanger for the partial oxidation of propane. Finally, the possibility of a temporary increase of the O/C ratio of the feed to remove the coke formed will be investigated.

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