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# Partial oxidation of methane over platinum metal gauze

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The partial oxidation of methane to synthesis gas has been studied over a platinum gauze catalyst. The experiments were carried out at atmospheric pressure with a single gauze in a quartz reactor heated in an electric furnace. The furnace temperature was varied in the range 200–900°C and the space time in the range 0.00021–0.00042 s. The feed consisted of a mixture of $CH_4 : O_2 : Ar \approx 2 : 1 : 10$ and carbon oxides and water were the main products. Oxygen was only partly consumed and relatively small amounts of hydrogen were formed.

**Keywords:** partial oxidation; Pt metal gauze; methane; synthesis gas

## 1. Introduction

Large resources of natural gas have made methane an important raw material for the chemical industry. Commercially, methane is mainly converted to chemicals and liquid fuels via synthesis gas. Steam reforming is the dominant process for the production of synthesis gas from hydrocarbons [1]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1)$$

An alternative way of producing synthesis gas from methane, is the direct partial oxidation [2]. Partial oxidation of methane would give a $H_2 : CO$ ratio of 2 in the ideal reaction:

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \qquad (2)$$

In practice some $CO_2$ and $H_2O$ are also formed by total oxidation [3]. Oxidation reactions are generally much faster than reforming reactions suggesting that synthesis gas could be produced directly in a relatively small oxidation reactor. A large research effort is presently being carried out on the catalytic partial oxidation of methane [2].

We have recently shown that high selectivities to CO and $H_2$ can be obtained by direct oxidation of $CH_4$ with $O_2$ over monolithic and fixed bed type of catalyst containing Ni, Pt, or Pd [4,5]. Product compositions close to equilibrium values were obtained in the temperature range 600–900°C. Yields of CO and $H_2$ close to equilibrium have also been reported from a number of other studies using similar catalysts [6–9].

Hickman and Schmidt [10,11] used a Pt–10%Rh gauze catalyst for partial oxidation of methane with air. They reported a complete conversion of oxygen even at very low space times with low $CH_4/O_2$ ratios. However, recent experiments with methane oxidation over a Pt gauze catalyst have indicated incomplete conversion of oxygen at very low space times and with a product gas composition far from equilibrium [5] as was also reported by Hickman and Schmidt [11]. Remarkably low selectivities to $H_2$ were observed during these preliminary runs [5]. The present work was initiated in order to study in more detail the partial oxidation of methane at very short contact times using a single Pt gauze catalyst. From a kinetic point of view incomplete conversion of oxygen is an interesting case, which also has some bearing on the product distribution.

## 2. Experimental

The experiments were carried out in a conventional flow apparatus using a quartz reactor with a Pt gauze catalyst. A circular Pt gauze was held between two cylindrical pieces of ceramic monoliths (Cordierite from Corning, 400 cells/in.$^2$) with a diameter of 15 mm. The monoliths were used as delivered by Corning without any washcoating. A schematic drawing of the reactor is shown in fig. 1. The gauze (1024 meshes/cm$^2$) was woven from a Pt wire of 60 μm diameter. The catalyst consists of only one layer of the Pt gauze with a diameter of 15 mm. The characteristics of the gauze catalyst is the same as for gauzes used in ammonia oxidation plants [12]. Initially the catalyst was treated in situ with $H_2$ at 600°C for 1.5 h.

The reactor was heated in an electric furnace. The axial temperature profile was measured at the center of the reactor by a movable thermocouple (chromel–alumel protected by a quartz tube). The catalytic experiments were performed at atmospheric pressure, the furnace temperature ($T_0$) was varied in the range 200–900°C and the space time ($\tau$) in the range 0.00021–

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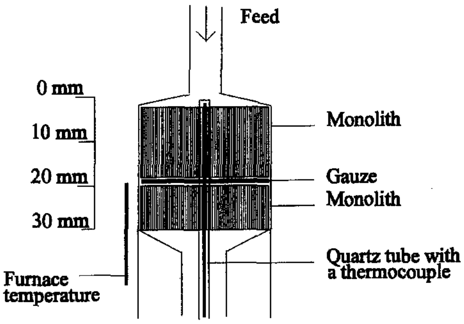

Fig. 1. Schematic drawing of the reactor. The diameter of the gauze and the monoliths is 15 mm.

0.00042 s (referred to 1 bar and 0°C). $T_0$ was measured by a thermocouple placed between the quartz reactor and the furnace at the position of the gauze as indicated in fig. 1. The space time is calculated from the free volume of the gauze (the open area of the gauze multiplied by the wire diameter) and the gas flow rate. The feed gas had a constant composition of $CH_4 : O_2 : Ar \approx 2 : 1 : 10$.

Conversion and selectivities were obtained by online GC analysis of the reactor effluent directly from the product gas analysis assuming no carbon formation or by using nitrogen as an internal standard. A two-column system with temperature programming and valve switching was used for the analysis on a HP 5890 gas chromatograph. Argon was used as the carrier gas, and $H_2$, $O_2$, $N_2$, $CH_4$, and CO were separated on a 25 m Molsieve 5 A capillary column. $CO_2$ and possible $C_2$ and higher hydrocarbons could be separated on a 25 m Poraplot capillary column. After separation the carbon oxides were hydrogenated to methane over a Ni catalyst at 375°C and detected on a FID.

## 3. Results and discussion

Previous experiments with empty quartz reactors with and without supports have shown that the conversion of $CH_4$ is low at temperatures below 800°C without a catalyst present [4]. With a Pt gauze as catalyst in the reactor, the effect of the furnace temperature on the conversion and the selectivity was investigated. The conversions of methane and oxygen and the selectivities of CO, $CO_2$, $C_2$ hydrocarbons and $H_2$ are shown in table 1. These experiments have been carried out continuously in the shown sequence with a new and reduced Pt gauze and with unused cordierite monoliths. The corresponding temperature profiles are given in fig. 2.

By increasing the furnace temperature from 20°C practically no conversion of methane was observed below 700°C. Heating between 700 and 800°C resulted in a sudden increase of the recorded reactor temperature of more than 150°C above the furnace temperature. As shown in fig. 2 the maximum increase in temperature is observed at the position of the Pt gauze. The temperature profiles indicate that the reaction mainly occurs on the gauze. It is reasonable to expect that the true temperature of the gauze is higher than the measured maximum temperature mainly because of the very small thickness of the gauze compared to the outer diameter (3 mm) of the quartz tube enclosing the thermocouple.

Table 1 shows that $O_2$ is only partly consumed at these very short space times. CO, $CO_2$ and $H_2O$ are the main products and surprisingly small amounts of $H_2$ are formed. Traces of $C_2$ hydrocarbons were detected at 800 and 900°C. During the runs reported in table 1 the furnace temperature is reduced from 900 to 200°C. The corresponding maximum gauze temperatures as measured by the thermocouple decreased from 1056 to 622°C. The large decrease in temperature has only a small effect on the conversions of methane and oxygen indicating a possible diffusion limitation of the rate. However, the ratio between CO and $CO_2$ decreases from 9.2 to 0.5 and the selectivity to $H_2$ decreases from 9.2 to 2.5 when the furnace temperature was decreased from 900 to 200°C.

Fig. 2 clearly indicates that the increase in the measured reactor (gauze) temperature relative to the furnace

Table 1

Conversions ($X$) of $CH_4$ and $O_2$ and selectivities ($S$) of CO, $CO_2$, $C_2$ hydrocarbons and $H_2$ over the Pt gauze at different furnace temperatures ($T_0$). Space time $\tau = 0.00021$ s. Feed $CH_4 : O_2 : Ar = 2 : 1 : 10$. The corresponding temperature profiles are shown in fig. 2

| $T_0$ (°C) | $X$ (%) | | $S$ (%) | | | |
|---|---|---|---|---|---|---|
| | $CH_4$ | $O_2$ | CO | $CO_2$ | $C_2$ | $H_2$ |
| 600 | 0 | 0 | – | – | – | – |
| 700 | 0 | 0 | – | – | – | – |
| 800 | 20.9 | 58.2 | 89.9 | 9.5 | 0.6 | 10.7 |
| 900 | 20.9 | 59.7 | 88.4 | 9.6 | 2.0 | 9.2 |
| 800 [a] | 17.7 | 54.6 | 79.7 | 19.8 | 0.5 | 5.2 |
| 600 [a] | 17.9 | 56.2 | 72.7 | 27.3 | 0 | 6.1 |
| 400 | 16.3 | 55.3 | 56.5 | 43.5 | 0 | 3.2 |
| 200 | 14.4 | 53.4 | 34.0 | 66.0 | 0 | 2.5 |
| 400 | 16.5 | 56.7 | 56.9 | 43.1 | 0 | 3.9 |
| 600 | 18.2 | 58.0 | 73.0 | 27.0 | 0 | 4.9 |
| 800 | 19.1 | 63.1 | 67.9 | 31.7 | 0.4 | 3.0 |

[a] Experiments representing temperature profiles at 800 and 600°C in fig. 2.

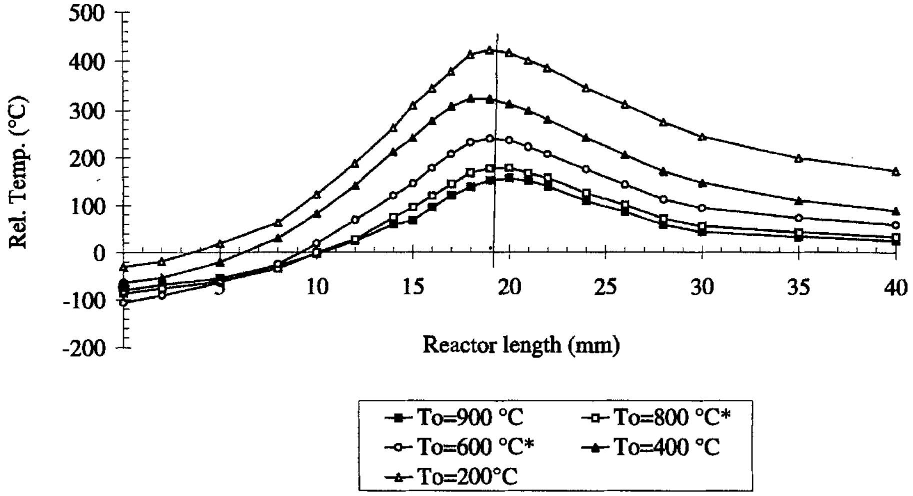

Fig. 2. Axial temperature profiles in the reactor as measured by the movable thermocouple relative to the furnace temperature $T_0$. The vertical line marks the position of the Pt gauze. Conditions as in table 1.

temperature is much higher at 200°C than at 900°C. This is in accordance with the change in the $CO/CO_2$ ratio and the lower selectivity towards $H_2$. The complete oxidations to $CO_2$ and $H_2O$ are strongly exothermal reactions which seems to become more important at lower temperatures.

In table 1 three runs are reported at 800°C. The first run shortly after the ignition of the reaction, the second after a decrease in the temperature from 900°C and the third after a stepwise increase in the furnace temperature from 200°C. The selectivity values for the three runs are significantly different, indicating that the selectivity changes with time on stream. This was further investigated by running the reaction over a new Pt gauze at constant temperature and space time for 480 min. The results are given in table 2 and the corresponding temperature profiles are shown in fig. 3.

The conversion of methane increased only slightly over the Pt gauze whereas the conversion of oxygen increased more distinctly (from 58 to 74%) with time on stream as shown in table 2. A pronounced change in the selectivities to products was also observed as a function of time on stream: $CO_2$ increased while CO, $H_2$, and $C_2$ hydrocarbons decreased. In particular, it is interesting to note the decrease in $H_2$ selectivity as a function of time on stream. After 480 min on stream the selectivity of $H_2$ is only 1.1%.

Fig. 3 shows that the temperature profiles in front of and at the gauze position are almost constant and independent of time on stream. However, downstream of the gauze and towards the reactor exit the temperature profiles become separated and in such a way that the longer the time on stream the higher the temperature. At times on stream longer than 400 min the measured reactor temperature even increases towards the reactor exit.

The increase in the temperatures measured close to

Table 2

Conversions ($X$) of $CH_4$ and $O_2$ and selectivities ($S$) of CO, $CO_2$, $C_2$ hydrocarbons and $H_2$ over a new Pt gauze as a function of time on stream. Furnace temperature $T_0 = 800°C$. Space time $\tau = 0.00021$ s. Feed $CH_4 : O_2 : Ar = 2 : 1 : 10$. The corresponding temperature profiles are given in fig. 3

| Time (min) | $X$(%) | | $S$(%) | | | |
|---|---|---|---|---|---|---|
| | $CH_4$ | $O_2$ | CO | $CO_2$ | $C_2$ | $H_2$ |
| 40 | 19.9 | 58.4 | 87.2 | 12.2 | 0.6 | 7.7 |
| 80 | 19.1 | 57.5 | 84.2 | 15.4 | 0.4 | 6.1 |
| 120 | 19.2 | 58.8 | 81.7 | 17.9 | 0.4 | 4.5 |
| 160 | 19.6 | 61.1 | 76.9 | 22.7 | 0.4 | 4.1 |
| 200 | 20.4 | 64.2 | 75.3 | 24.3 | 0.4 | 3.4 |
| 240 | 20.4 | 65.8 | 70.8 | 28.8 | 0.4 | 2.7 |
| 280 | 20.8 | 67.7 | 70.0 | 29.6 | 0.4 | 1.9 |
| 320 | 21.2 | 69.1 | 69.2 | 30.4 | 0.4 | 2.1 |
| 360 | 21.6 | 70.8 | 68.5 | 31.3 | 0.2 | 1.7 |
| 400 | 21.7 | 71.8 | 66.0 | 33.9 | 0.1 | 1.8 |
| 440 | 22.1 | 73.5 | 64.1 | 35.8 | 0.1 | 1.5 |
| 480 | 21.9 | 74.4 | 60.3 | 39.6 | 0.1 | 1.1 |

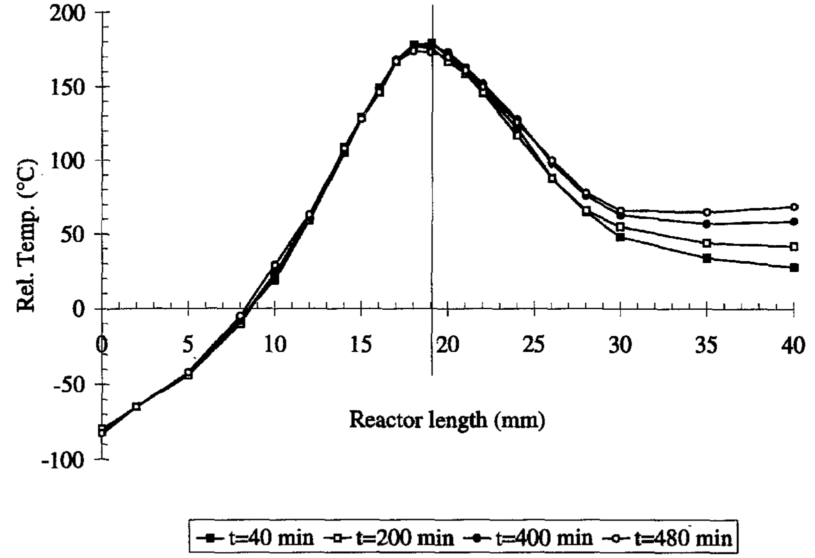

Fig. 3. Axial temperature profiles in the reactor as measured by the movable thermocouple relative to the furnace temperature $T_0$ at different times on stream. The vertical line marks the position of the Pt gauze. Conditions as in table 2.

the reactor exit at longer times on stream may be explained by the increased production of $CO_2$ and $H_2O$ (as shown in table 2). The temperature profiles given in fig. 3 are a strong indication that oxidation also occurs separated from the gauze. Other solid surfaces, e.g. the monolith or the reactor wall may after some time become contaminated with small amounts of Pt. Transport of Pt from a gauze catalyst is a well-known phenomenon in ammonia oxidation plants [13]. In this way additional catalytic activity may be developed in the reactor. These results indicate that part of CO formed on the Pt gauze at high temperature is subsequently oxidized to $CO_2$ in the reactor. The low selectivity to $H_2$ indicates that $H_2O$ is mainly formed on the Pt gauze at these conditions.

The space time was also varied over a Pt gauze catalyst at a furnace temperature of 800°C. The results are shown in table 3 and the corresponding recorded temperature profiles are given in fig. 4. The Pt gauze had been used prior to the experiments reported in table 3. Increasing the space time by a factor of two gave some increase in the conversion of oxygen and a smaller increase in the conversion of methane. However, there were only small changes in the selectivity to carbon oxides. The selectivity to $H_2$ was very low and in fact the selectivity approached zero as the space time (and the time on stream) increased. It should also be mentioned that at higher space times (0.00055 s, not incuded in table 3 and fig. 4) some carbon was formed.

Fig. 4 shows that a larger gas flow gives a higher peak temperature in the reactor as more heat is generated by the reaction. As the product gas is approaching the reactor outlet, the temperature profiles are levelling out. However, a larger flow rate gives a higher temperature level at the exit of the reactor. This could be an indication of additional catalytic activity in the reactor (the monolith or the wall after the gauze) as discussed above. It could also be explained by heat transport due to a generally higher temperature in the reactor at shorter space times. Even if CO may be a primary product [11,14] a shorter space time did not increase its selectivity probably because of the higher temperature which will increase the rate of the secondary oxidations.

Table 3

Conversions ($X$) of $CH_4$ and $O_2$ and selectivities ($S$) of CO, $CO_2$, $C_2$ hydrocarbons and $H_2$ over a used Pt gauze at different space times ($\tau$). Furnace temperature $T_0$ = 800°C. Feed $CH_4 : O_2 : Ar = 2 : 1 : 10$. The corresponding temperature profiles are given in fig. 4

| Space time (s) | $X$(%) | | $S$(%) | | | |
|---|---|---|---|---|---|---|
| | $CH_4$ | $O_2$ | CO | $CO_2$ | $C_2$ | $H_2$ |
| 0.00021 | 20.8 | 71.7 | 55.4 | 44.2 | 0.4 | 1.0 |
| 0.00021 | 21.0 | 72.7 | 53.8 | 45.8 | 0.4 | 0.8 |
| 0.00028 | 21.9 | 76.9 | 52.4 | 47.3 | 0.3 | 0.3 |
| 0.00028 | 23.3 | 81.7 | 53.0 | 46.8 | 0.2 | 0.4 |
| 0.00028 | 23.3 | 81.7 | 53.0 | 46.8 | 0.2 | 0 |
| 0.00042 | 24.3 | 86.7 | 55.6 | 44.2 | 0.2 | 0 |
| 0.00042 | 24.8 | 87.6 | 59.4 | 40.6 | 0 | 0 |

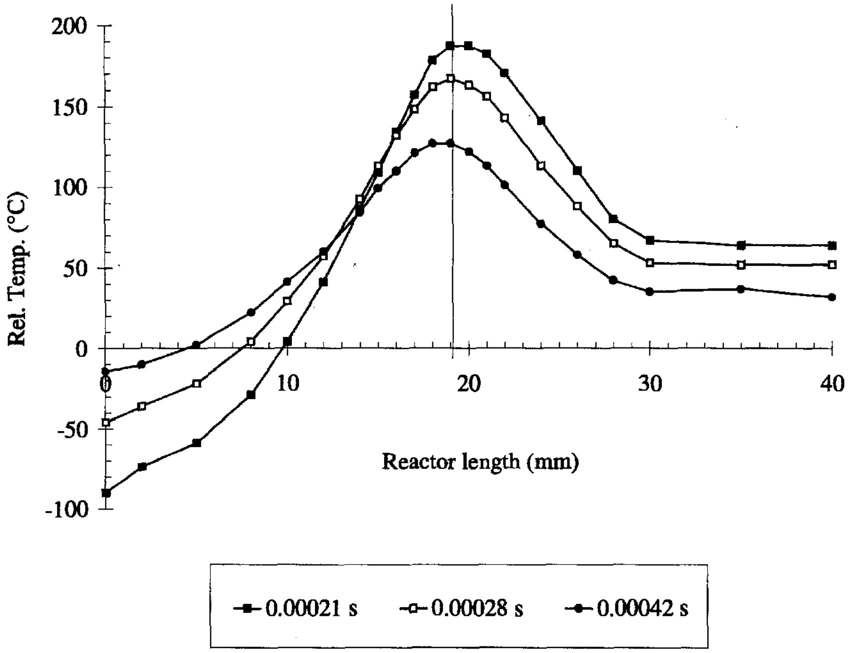

Fig. 4. Axial temperature profiles in the reactor as measured by the movable thermocouple relative to the furnace temperature $T_0$ at different space times $\tau$. The vertical line marks the position of the Pt gauze. Conditions as in table 3.

Different conclusions have been drawn as to the mechanism of CO and $H_2$ formation. According to Hickman and Schmidt [11,14,15], CO and $H_2$ are formed as primary products on Pt/10%Rh gauzes. A similar conclusion was drawn by Mallens et al. [16] for methane oxidation over Pt in the presence of $O_2$. The experiments were done in a TAP reactor by pulsing $CH_4 + O_2$ simultaneously over the catalyst. Buyevskaya et al. [17] consider CO as a secondary product formed from $CO_2$ and surface carbon on supported Rh catalysts. $H_2$ can be formed as a primary product by dehydrogenation of $CH_4$ on reduced Rh surfaces whereas $H_2O$ is formed on the oxidized surfaces. Analogous results were also obtained for supported Pd, Ru and Pt [17].

Partial oxidation of methane at relatively long contact times as in previous experiments [5], can be described as a total oxidation of part of the methane followed by reforming and the water–gas shift reactions. However, it is reasonable to believe that, at the short contact times obtained by using a gauze catalyst, the partial oxidation can be examined without being influenced to any large extent by secondary reactions [15].

At the short contact times used in this study the conversion of $O_2$ is limited to 50–60% in most cases. The high selectivity to CO at least at the highest temperatures as shown in table 1, support the idea that CO is formed as a primary product. Dehydrogenation of adsorbed $CH_x$ species gives hydrogen which may oxidize directly to water. It must, however, be emphasized that accessible $O_2$ at or close to the surface is controlled by transport limitations and more so the higher the temperature.

## 4. Conclusion

Partial oxidation of methane has been studied on a Pt gauze catalyst under conditions where the conversion of $O_2$ was not complete. The results show that at these very low space times high selectivities of CO are obtained, but low selectivities of $H_2$ even at temperatures above 800°C. A gradual change from CO to $CO_2$ is observed when the temperature decreases. The selectivity of $H_2$ and of CO decreased with the time on stream, whereas the conversion of methane increased only very slightly indicating secondary oxidation downstream of the Pt gauze.

## Acknowledgement

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