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Partial oxidation of methane to synthesis gas over a Pt / 10% Rh gauze

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The partial oxidation of methane to synthesis gas has been studied over a Pt / 10% Rh gauze catalyst. The experiments were carried out at atmospheric pressure using a single gauze in a quartz reactor heated in an electric furnace. The furnace temperature was varied in the range 200–1050°C and the space time in the range 0.00015–0.0005 s. The feed consisted of a mixture of $CH_4 : O_2 : Ar \approx 2 : 1 : 10$ and oxygen was only partly consumed. The products were carbon oxides, water, hydrogen and traces of C_2-hydrocarbons with compositions far from equilibrium. Compared to a Pt metal gauze a higher methane conversion and more favourable selectivities of synthesis gas, and in particular of H_2, were obtained at similar furnace temperatures. The Pt / 10% Rh gauze showed a better stability with time on stream compared to the Pt gauze. No loss of metal was observed from the Pt / 10% Rh gauze after 8 h on stream. The oxidation reactions were studied separately from steam reforming and the water–gas shift reaction at temperatures up to 1050°C at a space time of 0.00021 s. At 960°C the results indicate that CO and H_2 are formed beside H_2O as primary products.

Keywords: partial oxidation, methane, synthesis gas, Pt / 10% Rh gauze

1. Introduction

Methane can be converted to fuels and chemicals in two ways, either via synthesis gas or directly to C_2-hydrocarbons or methanol. In spite of large research efforts in developing a direct conversion process, no real breakthrough has been made so far. Commercial processes for methane conversion are therefore mainly based on synthesis gas. Steam reforming is the dominant process for production of synthesis gas from hydrocarbons [1].

An alternative way of producing synthesis gas from methane is the direct partial oxidation [2,3]. Partial oxidation will give a $H_2 : CO$ ratio of 2 in the ideal reaction:

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

In practice, some CO_2 and H_2O are also formed by total oxidation. Although this partial oxidation is only slightly exothermic, large temperature gradients may still exist in the catalyst bed since the reaction often consists of a total oxidation of some of the methane followed by endothermic reforming reactions and the water–gas shift reaction [4–6]. Oxidation reactions are generally much faster than the reforming reactions suggesting that synthesis gas could be produced in smaller reactors using oxygen instead of steam. A large research effort is presently being carried out on the catalytic partial oxidation of methane to synthesis gas [2].

Previous experiments [7] using Pt gauze as a catalyst for the partial oxidation of methane have shown that high selectivities of CO, but very low selectivities of H_2 are obtained at short reaction times where the conversion of O_2 is not complete. These results support the idea that CO is formed as a primary product at least at high temperatures. However, recent experiments [8] using Pt-impregnated monoliths indicate that both CO_2 and H_2O could be regarded as primary products under these conditions with short reaction times, high temperatures and incomplete O_2 conversion. Different conclusions have recently been reported as to the mechanism of the formation of synthesis gas [2–14] on Pt and Rh catalysts.

Rh-impregnated monoliths [8] gave substantially higher selectivities to H_2 compared with Pt-impregnated monoliths as first reported by Hickman and Schmidt [9]. In addition, Rh monoliths are more active for the oxidative methane conversion than the corresponding Pt monoliths [8]. Hickman and Schmidt [9] studied the partial oxidation of methane with air on Pt / 10% Rh gauze catalysts. O_2 was always completely converted and they reported high selectivities to CO and H_2 at short contact times using CH_4 / O_2 ratios lower than 2 : 1.

During previous experiments [7] with Pt gauze catalysts it was observed that the selectivity of the main products CO and H_2 changed with time on stream. After having been exposed to CH_4 / O_2 mixtures at high temperatures, the Pt gauze became brittle. The present study was initiated in order to investigate the stability of the Pt / 10% Rh gauze catalyst and the product distribution

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at the same conditions as was used previously [7] for Pt gauze catalysts. It is known [15] that the loss of Pt from gauze catalysts can be reduced by alloying Pt with Rh. Pt/10% Rh gauze catalysts should also give higher selectivities to H_2 compared with the Pt gauze. 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 [9].

2. Experimental

The experiments were carried out in a conventional flow apparatus using a quartz reactor with a Pt/10% Rh gauze catalyst. A circular 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 presented elsewhere [7]. The Pt/10% Rh gauze (1024 meshes/cm^2) was made of a 60 μm diameter wire. The catalyst consisted of only one layer of the gauze with a total diameter of 15 mm. 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 centre 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 200–1050°C and the space time (τ) in the range 0.00015–0.0005 s. The furnace temperature T_0 was measured by a thermocouple placed between the quartz reactor and the furnace at the position of the gauze. 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 (referred to 1 atm and 0°C). The feed gas had a constant composition of $CH_4 : O_2 : Ar \approx 2 : 1 : 10$.

Conversion and selectivities were obtained from online GC analysis of the reactor effluent using nitrogen as an internal standard or directly from product analysis assuming no carbon formation. A two-column system with temperature programming and valve switching was used for the analysis on a HP 5890 GC. 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

The effect of varying the furnace temperature on the conversions and the selectivities was investigated on the Pt/10% Rh gauze catalyst. The conversion of methane and oxygen and the selectivities to 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/10% Rh gauze and with unused cordierite monoliths. The corresponding temperature profiles as measured by the moveable thermocouple are given in figure 1.

By increasing the temperature from 20°C practically no conversion of methane was observed at furnace temperatures below 900°C. However, after 10 min at 900°C a sudden increase of the recorded reactor temperature

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/10% Rh gauze at different furnace temperatures (T_0) and gauze temperatures (T_g). Space time $\tau = 0.00021$ s. Feed $CH_4 : O_2 : Ar \approx 2 : 1 : 10$. The corresponding temperature profiles are shown in figure 1

T_0 (°C)	T_g (°C)	X CH_4 (%)	X O_2 (%)	S CO (%)	S CO_2 (%)	S C_2 (%)	S H_2 (%)
600	600	0	0	0	0	0	0
700	700	0	0	0	0	0	0
800	800	0	0	0	0	0	0
900 [a]	–	–	–	–	–	–	–
800 [b]	1000	29.5	74.5	96.1	3.6	0.3	28.7
900	1070	33.0	78.9	96.3	2.7	1.0	33.9
800	1000	29.0	74.3	95.8	3.9	0.3	26.6
600	860	23.8	70.8	87.7	12.3	0	10.4
400	740	21.6	69.9	73.2	26.8	0	4.2
200	650	20.3	69.7	55.9	44.1	0	2.2
400	740	22.0	70.9	73.7	26.3	0	4.8
600	860	23.9	71.2	87.6	12.4	0	10.0
800	1000	28.2	74.3	95.5	4.2	0.3	24.2
800	1000	28.2	74.0	95.6	4.1	0	24.3

[a] The reaction started after 10 min on stream at $T_0 = 900$°C. The furnace temperature was then lowered to 800°C before the product gas was analysed.

[b] This experiment corresponds to the temperature profile in figure 1.

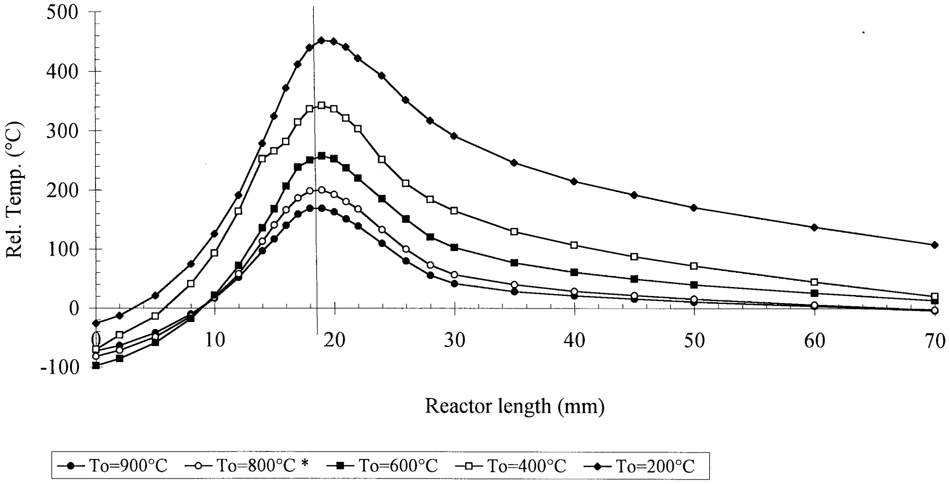

Figure 1. Axial temperature profiles in the reactor as measured by the movable thermocouple relative to the furnace temperature T_0 with space time $\tau = 0.00021$ s. The vertical line marks the position of the Pt/10% Rh gauze. Conditions as in table 1.

was observed as the surface reaction was ignited. The furnace temperature (T_0) was then reduced to 800°C and the product gas was analysed. As shown in table 1 the resulting conversions of CH_4 and O_2 were 29.5 and 74.5% respectively and the corresponding selectivities to CO and H_2 were 96.1 and 28.7%. As shown in figure 1 the maximum (peak) reactor temperature (~ 1000°C) is observed exactly at the position of the Pt/10% Rh gauze.

Table 1 shows that O_2 is only partly consumed at these very short space times. Traces of C_2-hydrocarbons were detected at 800 and 900°C. During the runs reported in table 1 the furnace temperature was reduced stepwise from 900 to 200°C. The corresponding maximum gauze temperatures as measured by the moveable thermocouple decreased from 1070 to 650°C. The large decrease in temperature did not have a pronounced effect on the conversions of methane and oxygen as shown in table 1. However, the ratio between CO and CO_2 decreased from 35.7 to 1.3 and the selectivity to H_2 decreased from 33.9 to 2.2% when the furnace temperature was reduced to 200°C. The small effect of the temperature on the conversion of methane and oxygen at this short space time indicates diffusion limitations of the rate.

Methane and oxygen are dissociatively adsorbed on the metal surface and H_2 and CO may be formed in the following reaction mechanism:

$$CH_{4(g)} \rightarrow CH_{x(s)} + (4-x)H_{(s)} \rightarrow C_{(s)} + 4H_{(s)} \quad (1)$$

$$O_{2(g)} \rightarrow 2O_{(s)} \quad (2)$$

$$2H_{(s)} \rightarrow H_{2(g)} \quad (3)$$

$$C_{(s)} + O_{(s)} \rightarrow CO_{(s)} \rightarrow CO_{(g)} \quad (4)$$

where (g) is gas and (s) is surface species. CO_2 and H_2O may be formed in the additional surface reactions:

$$H_{(s)} + O_{(s)} \rightarrow OH_{(s)} \quad (5)$$

$$OH_{(s)} + H_{(s)} \rightarrow H_2O_{(s)} \rightarrow H_2O_{(g)} \quad (6)$$

$$CO_{(s)} + O_{(s)} \rightarrow CO_{2(s)} \rightarrow CO_{2(g)} \quad (7)$$

The dissociative adsorption of methane (1) is an activated reaction on platinum and rhodium. For the activation energy of reaction (1) Hickman and Schmidt [16,17] used the values of 43.1 and 20.9 kJ/mol for Pt and Rh respectively. The chemisorption of oxygen is supposed to be non-activated on both metals. The relative concentration of oxygen on the surface will decrease at higher temperatures explaining the higher selectivities to CO and H_2.

The experiments show that the Pt/10% Rh gauze gives a higher methane conversion and is more selective to synthesis gas than the Pt gauze [7] at similar furnace temperatures. Hickman and Schmidt [9,18] studied the partial oxidation of methane to synthesis gas over Pt/10% Rh gauzes. However, the experiments were performed at slightly different conditions using one to five layers of gauze at 1227°C. The CH_4/O_2 feed ratio was 0.97 and 1.2 and with a contact time at a single layer of gauze of less than 0.0001 s. At a feed ratio of 0.97 all oxygen was consumed within one layer of gauze and the methane conversion was more than 90% with CO and H_2 selectivities of 90 and 40%, respectively. Increasing the CH_4/O_2 feed ratio to 1.2 reduced the methane conversion to 70% and gave CO and H_2 selectivities of 95 and 30%, respectively [9,18]. Our experiments showed a lower CH_4 conversion which is probably due to the higher CH_4/O_2 ratio employed, an incomplete conversion of O_2 and a lower temperature. However, the selectivities of CO and H_2 are almost equal to those of Hickman and Schmidt.

Concerning partial oxidation of methane to synthesis gas on Pt gauzes no data has been found in the literature.

It has been reported, however, that Rh-impregnated monoliths are significantly better catalysts than Pt-impregnated monoliths in producing CO and H_2 by the direct catalytic oxidation of methane [17]. The effect is most pronounced for the H_2 selectivity, as it is also observed in our experiments. It is argued [17] that the superiority of Rh over Pt is caused by one of the surface reaction steps involving OH which is slower on Rh than on Pt. Laser induced fluorescence spectroscopy has shown that the formation of OH has activation energies of 83.7 and 10.5 kJ/mol on Rh and Pt, respectively. According to Hickman and Schmidt [17] other reaction steps could also explain some of the difference. As the methane adsorption is an activated process the methane dissociation on the surface accelerates exponentially with increasing temperature. The ratio of adsorbed methane species (CH_x) and hydrogen adatoms to oxygen adatoms will therefore increase with increasing temperature. As this ratio increases the selectivity increases for CO and H_2 versus CO_2 and H_2O, as can be seen from the above reaction mechanism.

In our experiments the relatively small amounts of Rh in the Pt gauze have a relatively large effect on the performance. It is a well-known fact that during NH_3 oxidation Rh is enriched in the surface [19–21]. Anderson [19] found the surface concentration of Rh to be 60–100% on a Pt/10% Rh gauze after being exposed to the reaction conditions. A similar effect could also be expected during partial oxidation of methane to synthesis gas.

Mallens et al. [22] compared Rh and Pt sponge catalysts during TAP (temporal analysis of product) experiments and found Rh to be more active and selective for syngas formation. The difference is explained by the difference in activation energies for methane dissociation, which was found to be 52 kJ/mol on Pt and 15 kJ/mol on Rh. Lapszewicz and Jiang [23] also stated that the overall selectivity is controlled by the apparent ratio of activated reactants on the catalyst surface, methane dissociation being the rate limiting step.

The temperature profiles (figure 1) strongly indicate that the reaction mainly occurs on the gauze and show that the increase in the measured reactor (gauze) temperature relative to the furnace 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 selectivity towards H_2. The complete oxidation to CO_2 and H_2O is a strongly exothermal reaction which seems to become more important at lower temperatures.

Temperature measurements at high temperatures are always very difficult. In addition to the moveable thermocouple, an optical pyrometer (Leeds & Northrup) was used to measure the gauze temperature. The results given in table 2 show that the temperature measured by the pyrometer is almost identical to the maximum temperature observed by the moveable thermocouple. It was not possible to observe any hot spots on the gauze surface by use of the pyrometer. The steady-state temperature of the reactor is a function of the heat input from the furnace, the heat generated by the reactions and the heat losses from the reactor. It is difficult to calculate the temperature profile from an energy balance because the heat losses are not known. However, it is possible to calculate an adiabatic temperature which gives the highest possible temperature in the reactor system. As shown in table 2 the calculated adiabatic temperature is much higher than the measured gauze temperature due to the simple fact that the reactor is not operated adiabatically.

Table 2
Maximum gauze temperature as measured by the moveable termocouple T_M and the optical pyrometer T_{OP}. T_0 is the furnace temperature and T_{AD} is the calculated adiabatic temperature based on conversions and selectivities as reported in table 1

T_0 (°C)	T_{AD} (°C)	T_M (°C)	T_{OP} (°C)
900	1377	1070	1075

In order to test the statement in the introduction that partial oxidation can be studied without being influenced by secondary reactions using gauze catalysts, separate experiments with steam, CO_2 and H_2 were carried out. 1050°C is about the maximum obtainable gauze temperature (limitations of the furnace) which can be used for testing the catalytic activity for the steam reforming and the water–gas shift reaction. At this temperature no reaction occurred (X $CH_4 < 1\%$) neither with an empty reactor nor over a Pt/10% Rh gauze catalyst using a feed consisting of $CH_4 : H_2O : Ar \approx 1 : 1 : 10$ at a space time $\tau = 0.00021$ s. The same experiments with a feed of $H_2 : CO_2 : Ar \approx 1 : 1 : 10$ gave very low conversions of CO_2 (X $CO_2 < 1\%$). By doubling the space time, the conversion of CO_2 increased to 2%. These experiments indicate that the influence of steam reforming and the water–gas shift reaction was very low at the present conditions. Therefore, it is concluded that CO and H_2 are primary products from partial oxidation of methane at 1050°C which is the calculated adiabatic temperature for $T_0 = 400$°C in table 1.

In table 1 five runs are reported at $T_0 = 800$°C. The first run prior to ignition shows no reaction. The second run shortly after the ignition of the reaction, the third run after a decrease in the temperature from 900°C and the fourth and fifth runs after a stepwise increase in the furnace temperature from 200°C give all almost identical selectivities. This is in contrast to the results obtained with the Pt gauze [7] which showed a rapid change in product selectivites with time on stream. The stability of the Pt/10% Rh gauze was studied in some more detail by running the reaction over a new gauze at constant temperature and space time for 480 min. The results are given in table 3 and the corresponding temperature profiles are shown in figure 2.

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 Pt/10% Rh gauze as a function of time on stream. Furnace temperature $T_0 = 800°C$ and gauze temperature $T_g \approx 1005°C$. Space time $\tau = 0.00021$ s. Feed $CH_4 : O_2 : Ar \approx 2 : 1 : 10$. The corresponding temperature profiles are given in figure 2

Time (min)	$X\,CH_4$ (%)	$X\,O_2$ (%)	$S\,CO$ (%)	$S\,CO_2$ (%)	$S\,H_2$ (%)	$S\,C_2$ (%)
30	28.2	72.2	96.3	3.7	27.6	0
60	27.8	71.8	96.2	3.8	27.1	0
90	27.7	71.2	96.3	3.6	27.0	0.1
120	27.6	71.1	96.1	3.9	26.9	0
150	27.4	71.1	96.0	3.9	26.7	0.1
180	27.5	70.7	96.0	3.9	26.5	0.1
215	27.5	70.9	96.0	3.9	26.8	0.1
250	27.4	71.1	96.0	3.9	26.3	0.1
285	27.4	71.4	95.9	4.0	26.1	0.1
315	27.4	71.2	96.0	4.0	25.9	0
345	27.1	71.0	95.9	4.1	25.4	0
380	27.2	70.9	95.8	4.1	25.2	0.1
410	27.0	70.8	95.8	4.1	25.3	0.1
440	27.0	70.9	95.8	4.2	25.1	0
480	27.5	70.5	95.7	4.2	25.2	0.1

As seen from the results in table 3, the conversions of methane and oxygen as well as the selectivities of CO, CO_2 and H_2 do not vary much although there is a small tendency of less H_2 production with increasing time on stream. After 480 min on stream the selectivities of CO and H_2 are 95.7 and 25.2% respectively. In the case of the Pt gauze [7] the selectivities to CO and H_2 decreased from 87.2 and 7.7% to 39.6 and 1.1% respectively after 480 min on stream.

Figure 2 shows that unlike the Pt gauze [7] the temperature profiles are independent of the time on stream. It is interesting to notice that the temperature downstream of the Pt/10% Rh gauze did not change during the experiment. For the Pt gauze the temperature increased behind the gauze and towards the reactor exit, which may indicate that oxidation also occurred separate from the gauze. The monolith and the reactor walls may after some time become contaminated with small amounts of Pt, giving a further oxidation of CO and H_2 and a possible CH_4 oxidation downstream of the gauze. The loss of metal from Pt gauze catalysts is a known phenomenon in ammonia oxidation plants [24]. The present results show that for the oxidation of CH_4 at high temperatures the Pt/10% Rh gauze is much more stable than the Pt gauze.

Scanning electron microscopy (SEM) images of Pt/

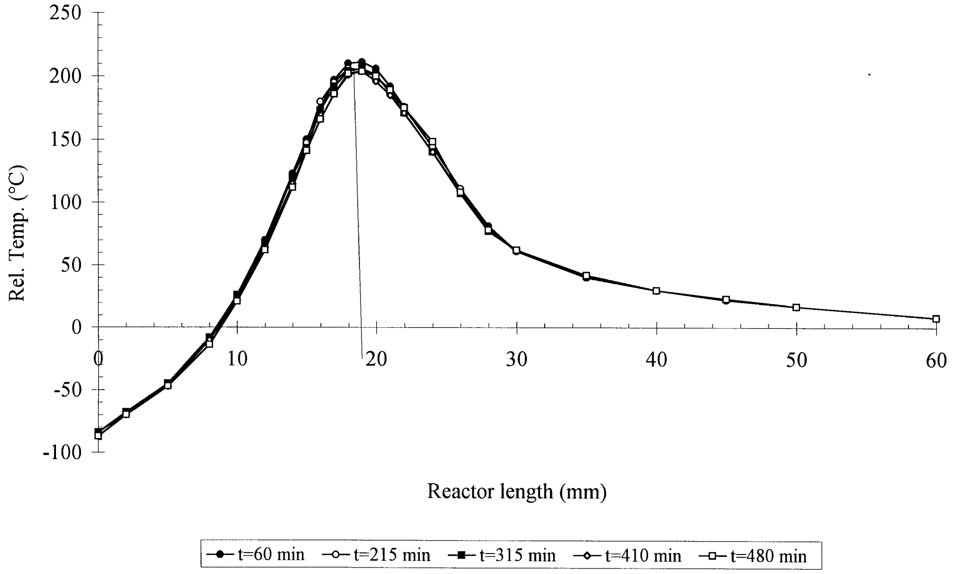

Figure 2. Axial temperature profiles in the reactor as measured by the movable thermocouple relative to a constant furnace temperature $T_0 = 800°C$ at different times on stream. The vertical line marks the position of the Pt/10% Rh gauze. Conditions as in table 3.

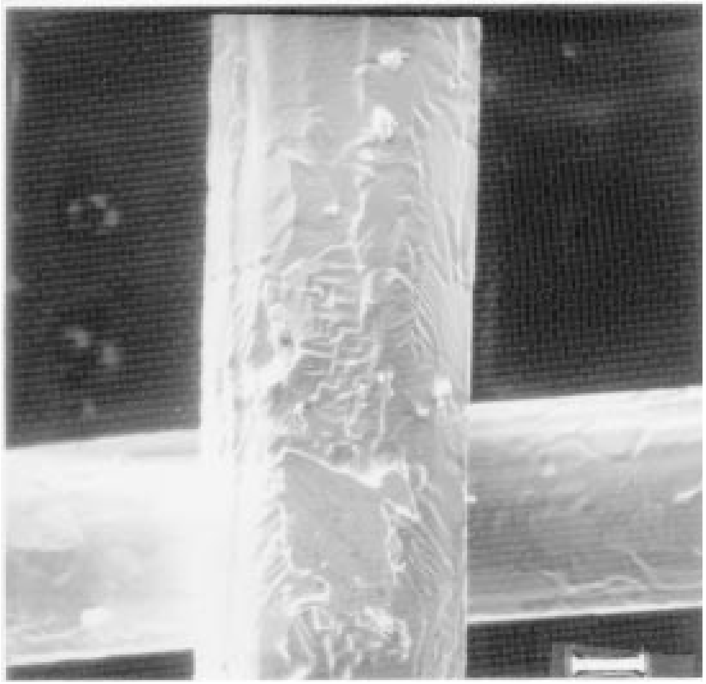

Figure 3. SEM image of the Pt/ 10% Rh gauze after 8 h on stream. The white bar equals 20 μm.

10% Rh and Pt gauze catalysts exposed to identical feed composition, time on stream and space time are given in figures 3 and 4. The SEM pictures of the two gauze catalysts show very different appearances. The Pt/ 10% Rh gauze (figure 3) showed some small restructuring after having been exposed to the experimental conditions given in table 3 for 8 h. This reconstruction is not like the cauliflower structures observed during ammonia oxidation giving a surface area of about 10 times higher than the initial area [21]. However, it could be the initial process of a similar reconstruction.

The surface of the Pt gauze catalysts has changed dramatically during operation (figure 4). However, it is impossible from the SEM images to conclude anything

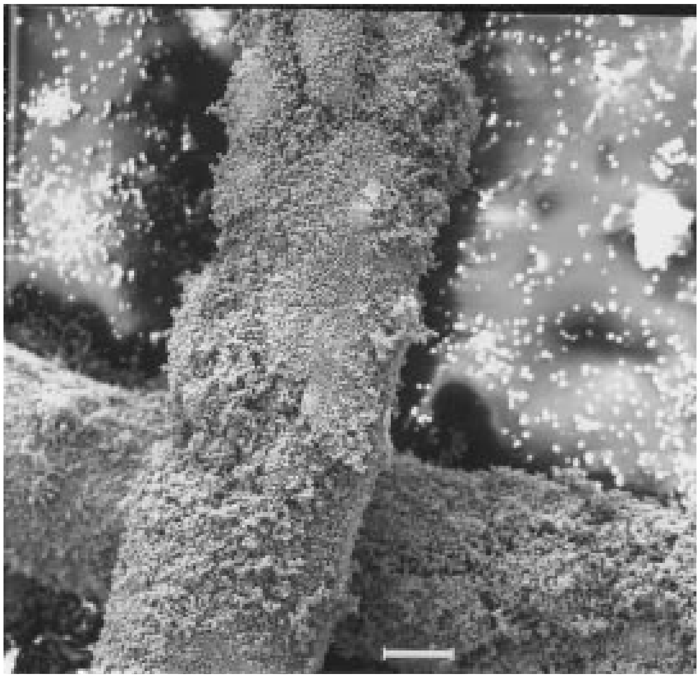

Figure 4. SEM image of the Pt gauze after 8 h on stream. The white bar equals 20 μm.

about the composition of the surface of the gauze catalyst. Most probably it consists of metal particles and possibly some small amounts of carbon. There will always be a risk of carbon formation when exposing methane to high temperatures. Wavelength dispersive X-ray spectrometer (WDS) analysis of the Pt gauze qualitatively showed carbon. Some particles were also found downstream of the Pt gauze, some in the monolith and some at the bottom of the quartz reactor. Energy dispersive X-ray spectrometer (EDS) analysis of these particles showed again Pt and carbon, supporting the theory of metal loss from the Pt gauze. A visual inspection of the gauze catalyst after use shows that it has changed colour to black/grey. This colour change can be attributed to carbon, but more likely it is platinum black. It should also be noted that the pure Pt gauze was very brittle after the reaction. By removing the gauze from the reactor it fell apart. This means that Rh possibly increase the mechanical strength of the metal gauze catalysts. The fact that Rh increases the mechanical strength of a Pt gauze is also known from NH_3 oxidation [24].

As already discussed, Hickman and Schmidt [18] have previously reported experiments on partial oxidation of methane over Pt/10% Rh gauzes. SEM images showed surface restructuring during the first few hours of use. Some of the gauze catalysts showed a large decrease in activity and selectivity to synthesis gas after being exposed to very high temperatures (> 1300°C) for several hours or after being tested over a wide range of feed conditions. The decrease in activity was accompanied by a change from a faceted surface morphology to smoother, rounded surface structures and pits. In contrast to our experiments restructuring was found over a Pt/10% Rh gauze. This could possibly be explained by the differences in the temperature and the length of operation. Goetsch et al. [25] have recently studied the partial oxidation of C_2 and higher alkanes over Pt/10% Rh gauzes. SEM images of the gauze showed a dramatic roughening of the surface upon exposure to partial oxidation conditions. A closer inspection of the surface revealed metal facets and EDX analysis indicated that the structures were metallic.

Surface restructuring and metal losses from Pt and Pt alloy gauzes in the highly oxidizing ammonia conversion reaction are thought to occur mainly by volatile metal oxide transport and surface diffusion [15,26–29]. Particles breaking off or hot spots close to the melting temperature may also be involved. Platinum oxides are formed at regions with a strong oxidizing potential and reduced and deposited in regions with more reducing conditions. According to MacCabe et al. [26,29] several processes occur on the gauze: (i) platinum oxide vapour formation, migration and decomposition, (ii) selective oxidation of rhodium species, (iii) thermal faceting, (iv) formation of grain boundary grooves, (v) surface diffusion and (vi) bulk diffusion in both metal and oxide. The extent of each process is dependent on the reaction conditions. If the temperature is too low, there is insufficient PtO_2 vapour pressure, and the dominant process is the selective oxidation of Rh to Rh_2O_3 giving a deactivated catalyst. If the temperature is too high surface and bulk diffusion is enhanced, leading to a smoothing out of the surface features. The lower rate of restructuring observed over a Pt/Rh gauze compared to a pure Pt gauze suggests that the partial vapour pressure of PtO_2 is lower over the alloy, explaining the reduced metal loss. Only within a certain range of conditions restructuring is leading to the "cauliflower" surface.

There are similarities between the restructuring and metal loss found in our experiments compared to what is known from ammonia oxidation. The fact that the gauzes during partial oxidation do not obtain the "cauliflower" structure may, according to the above discussion, be explained by the higher temperature employed. The lack of reconstruction and metal loss from the Pt/10% Rh gauze observed in our experiments are probably due to the relatively short time on stream (8 h). According to Rubel and Pszonicka [30] Rh which is enriched on the surface, forms the nonvolatile Rh_2O_3. This could be a possible explanation for the reduced metal loss in alloyed gauzes.

In spite of the fact that Pt by most authors is believed to be lost from the catalyst as PtO_2 [15,26–29] there could also be other explanations. According to Kummer [31] platinum oxides are not stable above ~ 500°C when heated in air. PtO_2 has a melting temperature of 450°C and PtO decomposes at 550°C while Rh_2O_3 decomposes at a temperature of 1100–1150°C [32]. The active surface of the Pt/Rh catalyst in NH_3 oxidation is found to be free of oxides except for Rh_2O_3 during operation [33]. Another possibility may be that the catalytic restructuring proceeds by formation and decomposition of short-lived radical species [34]. The catalytic restructuring was investigated on Pt foils in a hydrogen–oxygen mixture. It was suggested that the restructuring is attributed to the interaction of homogeneously formed radicals, most likely HO_2, with the platinum surface, and a subsequent evaporation of metastable platinum-containing species.

It should also be noted that the different metal gauze catalysts showed different ignition temperatures. The feed mixture was admitted to the catalyst at 600°C immediately after H_2 reduction. The temperature of the furnace was increased continuously and the gauze temperature followed closely. Then at a certain temperature, different for the two gauzes, the reaction ignited leading to a very fast increase of the reaction temperature, which became 150°C or more above the furnace temperature. The ignition temperature for the pure Pt gauze was observed at 800°C, while the Pt/10% Rh gauze needed a temperature of 900°C to ignite. The reason for this difference could be the fact that rhodium oxide has to be reduced or decomposed before ignition. A higher amount of Rh will then give a higher ignition temperature. Farrauto and Lee [35] showed that platinum could

Table 4
Comparison of fresh and used (8 h on stream) Pt/10% Rh gauze and Pt gauze catalysts using a feed of $CH_4 : O_2 : Ar \approx 2 : 1 : 10$ at a space time of 0.00021 s

Metal gauze	T_0 (°C)	T_g (°C)	$X\,CH_4$ (%)	$X\,O_2$ (%)	$S\,CO$ (%)	$S\,CO_2$ (%)	$S\,H_2$ (%)	$S\,C_2$ (%)
Pt/10% Rh (fresh)	800	1015	28.2	72.2	96.2	3.7	27.6	0
Pt (fresh)	800	980	19.9	58.4	87.2	12.2	7.7	0.6
Pt/10% Rh (8 h)	800	1010	27.5	70.5	95.7	4.2	25.2	0.1
Pt (8 h)	800	973	21.9	74.4	60.3	39.6	1.1	0.1

be electrostatically deposited on a new Pt/Rh gauze to increase the surface area. During the early stages of the NH_3 oxidation process, the activity gradually increases in parallel with the growth in catalytic surface area of the gauzes. By increasing the originally surface area the time needed to obtain an active catalyst decreased. Another interesting observation was the lowering of the ignition temperature with increasing surface area. This effect could possibly be coupled to the fact that the modified surface contains more platinum and less rhodium.

A summary of the results obtained with the Pt/10% Rh gauze and the previous results with the Pt gauze is given in table 4. For the fresh catalysts, the Pt/10% Rh gauze is more active and more selective for the formation of synthesis gas. It should be noted that the temperature of the Pt/10% Rh gauze is about 35°C higher than the temperature of the Pt gauze. However, as already discussed small temperature variations show very small effects on the product composition. The conversion of CH_4 is 28% with the Pt/10% Rh gauze and only 20% with the Pt gauze. A reduction in selectivity of CO and H_2 is observed when changing catalyst from a Pt/10% Rh gauze to a Pt gauze. After 8 h on stream the differences between the two gauze catalysts are even larger due to the metal loss and surface restructuring of the Pt gauze.

The most stable catalyst, the Pt/10% Rh gauze, was investigated as a function of space time at a constant measured temperature of 960°C. The feed composition was as in previous experiments: $CH_4 : O_2 : Ar \approx 2 : 1 : 10$. The results are shown in figure 5. The selectivities to CO and H_2 increase with decreasing space time with a corresponding decrease in CO_2 and H_2O formation. The results clearly indicate CO, H_2 and H_2O as primary products. At short space times oxygen is only partly consumed. Under such conditions with very fast surface reactions the transport of reactants to the surface may limit the rate. O_2 may be more diffusion limited than CH_4 because of the higher molecular weight. Diffusion limitations will therefore decrease the relative concentration of oxygen on the catalyst surface. Shorter space times giving less oxygen on the surface will according to the proposed mechanism (eqs. (1)–(7)) produce more H_2 and CO and less H_2O and CO_2.

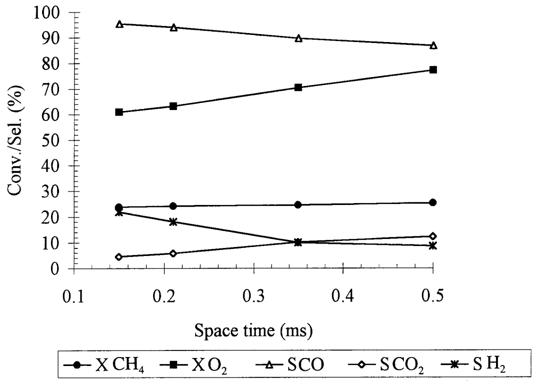

Figure 5. Conversions (X) and selectivities (S) as a function of space time at a measured gauze temperature of 960°C over a Pt/10% Rh gauze. Feed: $CH_4 : O_2 : Ar \approx 2 : 1 : 10$.

4. Conclusion

The partial oxidation of methane to synthesis gas has been studied over a Pt/10% Rh gauze at conditions where the conversion of O_2 was not complete. The results are compared with previous results on a Pt gauze. The Pt/10% Rh catalyst gives a higher conversion of methane and more favorable selectivities to CO and H_2. The Pt/10% Rh catalyst is more stable with time on stream. No loss of metal was observed from the Pt/10% Rh gauze after 8 h on stream. Steam reforming and the water–gas shift reaction are not occurring at temperatures below 1050°C at a space time of 0.00021 s. Results at 960°C indicate that CO and H_2 are formed beside H_2O as primary products on the Pt/10% Rh catalyst.

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