Partial oxidation of methane to synthesis gas over Rh/α-Al_2O_3 at high temperatures

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The partial oxidation of methane to synthesis gas has been studied in a continuous flow reactor using a Rh/α-Al_2O_3 catalyst under conditions as close as possible to those industrially relevant: pressures up to 800 kPa and temperatures higher than 1274 K in order to avoid the formation of carbon and to obtain high equilibrium selectivities to CO and H_2. Intrinsic kinetic data were obtained when the feed was diluted with helium. Gas-phase reactions were found to occur at 500 kPa when the feed was not diluted. A reaction network has been derived from experimental results in which oxygen conversions range from 0 to 1. CO_2, C_2H_6 and H_2O are the primary products. C_2H_4 is formed by oxidative dehydrogenation of C_2H_6. CO and H_2 are formed by reforming of CH_4 by CO_2 and H_2O; an additional direct route to CO and H_2 at low oxygen conversions cannot be excluded. The catalyst appears to be present in two states, the transition being at an oxygen conversion of 0.4 under the conditions used. The support probably enhances oxidation reactions by reverse spillover of oxygen or hydroxyl species onto rhodium. The support as such behaves similarly to the catalyst at low oxygen conversions, but shows no reforming activity.

Keywords: partial oxidation, methane, synthesis gas, Rh/α-Al_2O_3

1. Introduction

The partial oxidation of methane with oxygen to synthesis gas has recently received increasing attention as an alternative to the steam reforming of methane. Several authors claim that over certain catalysts this reaction can proceed directly to yield CO and H_2 [1–4]. However, it has been shown by other authors [5–8], that over a variety of catalysts an indirect route is followed: first all the oxygen is used up for the complete combustion of part of the methane, and subsequently the residual methane is reformed by steam and CO_2. Such an indirect route would result in an axial temperature profile in a continuous flow reactor, with very high temperatures at the entrance of the catalyst bed, which has detrimental effects on the catalytic material and causes difficulty with respect to heat management.

This paper describes a kinetic study using Rh/α-Al_2O_3. Preliminary experiments have shown that it gives good selectivities to CO and H_2, although the catalyst deactivated at temperatures below 1274 K, which is probably due to the deposition of carbon, as has also been reported for other metals [9]. Thermodynamic calculations showed that, under the experimental conditions used, graphitic C is not stable at a temperature higher than 1274 K, and the use of such high reaction temperatures can thus help to avoid coke formation. Temperatures above 1274 K are also favourable for the formation of CO and H_2, their selectivities at equilibrium being greater than 0.99 at the pressures used in the present paper.

At such high temperatures gas-phase reactions may become important. Chen et al. [10] developed a model for gas-phase chain reactions under conditions used for the oxidative coupling of methane. Furthermore, it is generally accepted, that in the oxidative coupling of methane CH_3 radicals are formed on the catalyst surface, which can dimerize in the gas-phase [11]. These processes may also be of importance for the catalytic partial oxidation of methane.

Many consecutive processes using the synthesis gas produced, such as methanol synthesis, operate at high pressures. It is most economical to compress at a stage in the process where the fewest molecules are present, which is prior to the partial oxidation. Therefore, industrial application of the partial oxidation process would preferably be operated at pressures around 2.5 MPa. At these high pressures the contribution of gas-phase chain reactions may be considerable.

Studies of catalytic partial oxidation on metallic Rh have been reported in the literature [1,12], which contributed significantly to the understanding of partial oxidation over Rh metal. However, the role of the support – usually alumina – was not clarified in these papers. Recently, Wang et al. [13] proposed that during pulse experiments using a TAP apparatus the reverse spillover of OH species from the support onto the rhodium affects the activity and selectivity. Supported rhodium is expected to behave differently to unsupported rhodium also at higher temperatures and pressures. This is part of

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the subject of the present paper. TAP studies have been performed [3,12] in which, at pressures around 0.1 kPa, the degree of oxidation of rhodium is reported to affect the activity and selectivity of the catalyst. It would be useful to be able to obtain information on the degree of oxidation under more realistic steady-state conditions.

The aim of the research described here is to obtain reliable kinetic information necessary for scale-up purposes. This paper therefore investigates (i) the reactions on the surface of the catalyst, both metal and support, and (ii) the influence of potentially important gas-phase reactions. This is done under conditions as close as possible to those industrially relevant, but under which it is still possible to obtain intrinsic kinetic data.

2. Catalysts

The catalyst was prepared by impregnating a low-surface-area α-Al_2O_3 support (Johnson-Matthey Alfa Products), which had previously been washed in boiling nitric acid (60%) and heated at 1123 K in order to remove impurities, with a solution of $Rh(NO_3)_3{\cdot}2H_2O$ (Johnson-Matthey Alfa Products). The impregnated material was dried at 373 K, heated at 473 K in a nitrogen flow, and reduced at 523 K first in a mixture of N_2 and H_2 and subsequently in a pure H_2 flow; it was cooled down to room temperature in a N_2 flow.

Table 1 summarizes the properties of the catalyst. The compositions of the catalyst and the support were chemically analysed. The major impurities found in the support after washing were Ca (1.3×10^{-2} wt%), K (7.0×10^{-3} wt%) and Fe (1.2×10^{-3} wt%). The surface areas of the catalysts were measured by chemisorption of CO (metal surface area) or physisorption of Kr (BET surface area), using a Micromeritics ASAP 2010C apparatus. The pore sizes and pore volumes were measured by mercury porosimetry.

Table 1
Properties of the fresh catalysts

Rh-loading (wt%)	0.3
fraction Rh exposed	0.016
Rh surface area ($m^2\ kg^{-1}$)	19
BET surface area ($m^2\ kg^{-1}$)	120
pore diameter (nm)	> 3000
pore volume ($m^3\ m^{-3}$)	< 0.05

3. Experimental setup

The experiments were performed in a continuous flow reactor setup. Prior to the catalytic measurements, the catalyst, or the support alone, was exposed in situ to a flow of 2% H_2/He and heated up to 1140 K with a heating rate of 3.2 K min^{-1}. After flushing with He for 15 min and heating up to 1200 K, the reactant mixture was admitted to the reactor. Both sintering and evaporation of rhodium during the kinetic study were reduced by pretreating the catalyst in the reactant mixture, consisting of $CH_4/O_2/He = 6.7/3.3/90$, at $T = 1400$ K and $p = 400$ kPa for 2 h; an oxygen conversion of 1 and a methane conversion of 0.75 were found under these conditions. He was 99.996% pure, and CH_4 and O_2 99.995%.

A sintered alumina tube-reactor was used. The reactor, as well as the sintered alumina pellets used for dilution or for filling empty space, were cleaned prior to the experiments in a 60% nitric acid solution followed by thorough washing with distilled water and subsequent heating in air at 1123 K in order to remove any impurities. The reactor could be pressurized up to 2.5 MPa using a back-pressure controller, and heated up to 1500 K by means of an electrical furnace. Several security devices were placed upstream the reactor, such as a pressure relieve valve, a flame extinguisher and a rupture disk, which would limit the damage in the case of explosion.

All the products could be analysed using two on-line HP 5890 series II gas chromatographs in series, equipped with Chrompack wide-bore molsieve-5A and poraplot-Q columns and TCD and FID detectors, using either He or Ar as carrier gas. N_2, with a well-known flow rate, was mixed with the reactor effluent before entering the GCs as an internal standard. The conversions of methane and oxygen were calculated by dividing the amounts found in the product mixture by the total number of moles of C and O($\times$2) in the product, respectively. The selectivities were based on the number of moles of C or, where appropriate, H in the specific component divided by the total number of moles of C or H in the product mixture. The balances for C, H and O always closed within 5%.

4. Reactor design and experimental conditions

Because of the exothermicity of the oxidation reactions, special precautions were taken in order to be able to measure the kinetics of the catalytic reaction under well-known experimental conditions.

Sintered alumina was used as material for both the reactor and the thermocouple well because of its inertness. The catalyst, diluted with inert non-porous alumina pellets with a diameter of 106–150 μm, was located in the centre of the reactor. At the top and the bottom of the catalyst bed, non-porous alumina spheres of 0.5–1.0 mm were placed in order to fill empty space without affecting the gas-flow regime.

A sintered alumina tube was placed at the bottom and also one at the top of the reactor, in order to fill as much empty space as possible, because at the high temperatures used, gas-phase reactions may become important. The homogeneous gas-phase model developed by

Chen et al. [10] has been modified using experimental data obtained in an empty reactor at the temperatures, pressures and flow rates used for CPO, and can thus accurately simulate gas-phase reactions under the conditions used in the present experiments. During most experiments the reactant gases were diluted with helium and experiments were performed in a limited pressure range; under these conditions very low conversions in the gas-phase were indeed predicted, being at most one tenth of the conversion found in the experiments described here.

Transport limitations may be important especially when highly exothermic or endothermic reactions occur, such as total combustion and reforming reactions. Although several experimental "diagnostic" tests for the occurrence of mass- and heat-transport limitations are available, they are difficult to apply in the present case. Therefore the criteria given by Mears [14–16] were applied. In these criteria the potential rates of chemical reaction are compared with those for mass- and heat-transport, both in the catalyst pellet (internal) and at the surface of the pellet (external). Also radial heat transport in the reactor was taken into account. The axial temperature profile was measured. Calculations performed for each experiment showed that these criteria were met by using small catalyst pellets (80–106 μm) with low metal loading, a small surface area and very large pores (see table 1), as well as high gas velocities (1–7 m s^{-1}) and helium as a diluent.

Plug flow was achieved by using small catalyst pellets and by a ratio of the reactor diameter over the catalyst pellet diameter greater than 10 [15]. The pellet diameter was, however, chosen to be sufficiently large to prevent the occurrence of a significant pressure drop over the catalyst bed. The diameter of the reactor was small, so as to minimize the radial temperature gradient over the catalyst bed; also, for the same reason, the catalyst bed was diluted with inert non-porous alumina in an amount which would, according to the criteria proposed by Van den Bleek et al. [17], not influence the conversions and selectivities. Axial temperature gradients over the catalyst bed [14] were suppressed by the use of a fluidised bed around the reactor, which improved the heat transfer between furnace and reactor. The temperature was measured by a thermocouple in a thermowell situated at the centre of the reactor, which could be moved up and down the reactor; a temperature gradient was found of at most 4 K over the catalyst bed under the conditions used, as is shown in fig. 1. This result shows that the precautions were effective, because, when using a feed which contained 90% He, adiabatic temperature increases of 60 to 520 K at 100% oxygen conversion were calculated, depending on the selectivities; a typical adiabatic temperature rise of 200 K was calculated for 90% selectivity to CO and H_2.

Experiments were also performed in order to investigate the effect, especially concerning gas-phase reactions, of using undiluted feed. These experiments were carried out using the support alone and at the relatively low temperature of 1060 K, in order to be able to maintain low conversions and corresponding heat effects.

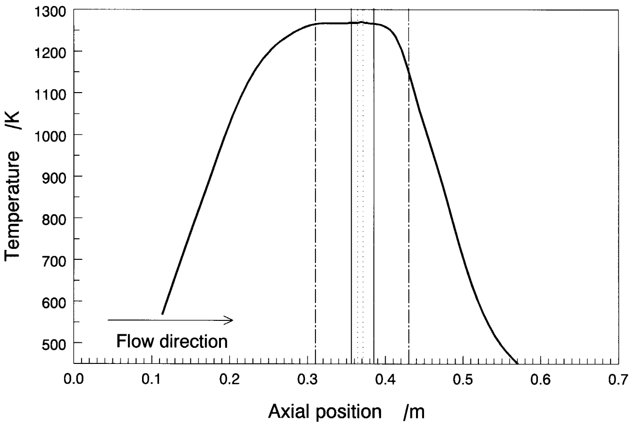

Fig. 1. Axial temperature profile in the reactor during catalytic experiments. (...) Position catalyst bed, (—) position inert alumina pellets, (- - -) position fluidised bed.

The experimental conditions are given in table 2.

5. Results

Table 3 gives the Rh contents of the catalysts at various stages during the experiments. After the pretreatment at 1400 K, 50% of the Rh had disappeared from the catalyst, probably by evaporation of RhO_2; from data supplied by Mallens et al. [3] a low but significant vapour-pressure (2×10^{-2} Pa) for RhO_2 was calculated at the temperature used during the pretreatment. The evaporation of Rh strongly depends on the temperature: after a treatment at 1273 K in flowing oxygen for 1 h followed by flowing hydrogen for 1 h, only 12% Rh had disappeared. When the catalyst was analysed after 15 days of experiments, the amount of Rh on the catalyst had further decreased, while a significant amount of Rh was found on the inert diluent. Whether the Rh was present on the catalyst or on the inert did not influence the catalytic performance, which under the reaction conditions was found to be stable for more than 15 days. However,

Table 2
Experimental conditions during experiments

temperature (K)	1060–1400
pressure (kPa)	140–800
total flow rate (10^{-3} mol s^{-1})	0.1–4.5
$W/F_{CH_4,0}$ (kg s mol^{-1})	0.2–3.0
residence time (10^{-3} s)	1–75
$CH_4/O_2\|_0$	1.0–4.0
$p_{CH_4,0}$ (kPa)	10–334
$p_{O_2,0}$ (kPa)	3–167
helium dilution (%)	0, 87–97
CH_4 conversion	0.0–0.8
O_2 conversion	0.0–1.0

Table 3
Percentage of the initial Rh-content found on the catalyst and on the inert material, dependent on the history of the samples

History of the catalyst	Rh on catalyst (% of initial content)	Rh on inert (% of initial content)	Rh disappeared (% of initial content)
fresh	100	0	–
treatment at 1273 K	88	–	12
pretreatment at 1400 K	50	4	46
catalytic test 15 days	28	22	50
catalytic test 27 days	11	18	71

when another catalyst sample was analysed after a series of 27 days of experiments, the amount of Rh found on both the catalyst and the inert had decreased to 29% of the initial content. Fig. 2 shows the conversions at reference experiments taken at regular intervals during the time of operation. During the first two days a significant deactivation was observed, thereafter the catalytic performance was stable.

Fig. 3 shows the conversions and selectivities on Rh/α-Al_2O_3 as a function of the space time, $W/F_{CH_4,0}$. The oxygen conversion varies from 0 to 1, which allows analysis of the complete reaction network. Two main regions can be distinguished in this figure: (i) $X_{O_2} < 0.4$ and (ii) $X_{O_2} = 1$. No data points could be obtained in the range $0.4 < X_{O_2} < 1$, where obviously the reaction rate accelerates significantly. In region (i) at the shortest space times used, CO_2, C_2H_6, and H_2O are found to be the major products. With increasing space time, the selectivities to CO_2, C_2H_6 and H_2O decrease, whereas those to C_2H_4, CO and H_2 increase. When the oxygen conversion approaches 100%, the selectivities to CO_2 and H_2O strongly increase, that to CO stays at a constant level, and those to C_2H_4 and H_2 drop to zero. Apparently, the oxidation reactions of CH_4, C_2H_4 and H_2 are strongly accelerated at this point. This is an intrinsic effect as a strong increase in the temperature was not observed. In region (ii) the selectivities to CO and H_2 increase rapidly with increasing space time towards their equilibrium values.

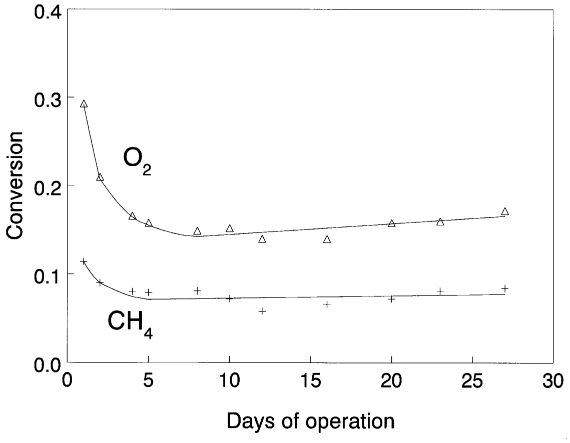

Fig. 2. Conversions on Rh/α-Al_2O_3 as a function of time of operation during reference experiments. $T = 1274$ K, $p = 400$ kPa, $CH_4/O_2/He|_0 = 6.7/3.3/90$.

The reaction rates increased with increasing pressure; the trends as shown in fig. 3 were also found at pressures up to 800 kPa. Variation of the partial pressures of CH_4 and O_2 at low oxygen conversions ($X_{O_2} < 0.25$) allowed to determine partial reaction orders of 0.5 in CH_4 and 0.4 in O_2. The addition of small amounts of CO_2 or H_2O did not affect the reaction rate.

Fig. 4 shows results obtained using the support alone. This figure very much resembles fig. 3; however, the conversions for the support are lower than half of those for the catalyst at comparable space times. Although at low conversions the trends in the selectivities are similar for the support and the catalyst, at higher conversions they differ clearly: neither the steep increase in O_2-conversion, nor the sharp maximum in the selectivities to CO_2 and H_2O, nor the subsequent rapid increase in selectivities to CO and H_2 were observed for the support.

Calculations showed that the results reported above were not influenced by mass- and heat-transport and that thus intrinsic kinetics were measured when the feed had been diluted with helium. Gas-phase reactions did not play a significant role when the feed was diluted with helium. The following experiments were carried out in order to investigate the significance of gas-phase reactions when the feed was not diluted.

The experiments with undiluted feed were performed using the support and at the relatively low temperature of 1060 K, at which no significant heterogeneous reactions could be observed. Table 4 compares the results of experiments at various pressures with those of simulations using the modified gas-phase model. At 500 kPa heat transport limitations occurred, leading to a radial temperature gradient which caused a deviation of the measured rates of more than 5%. At the relatively low pressure of 140 kPa the experimentally observed conversions are only one third of those predicted by the gas-phase model and the observed selectivities also differ significantly from those predicted. However, at 500 kPa the experimental results are rather close to those simulated.

6. Discussion

From the experimental data some interesting qualita-

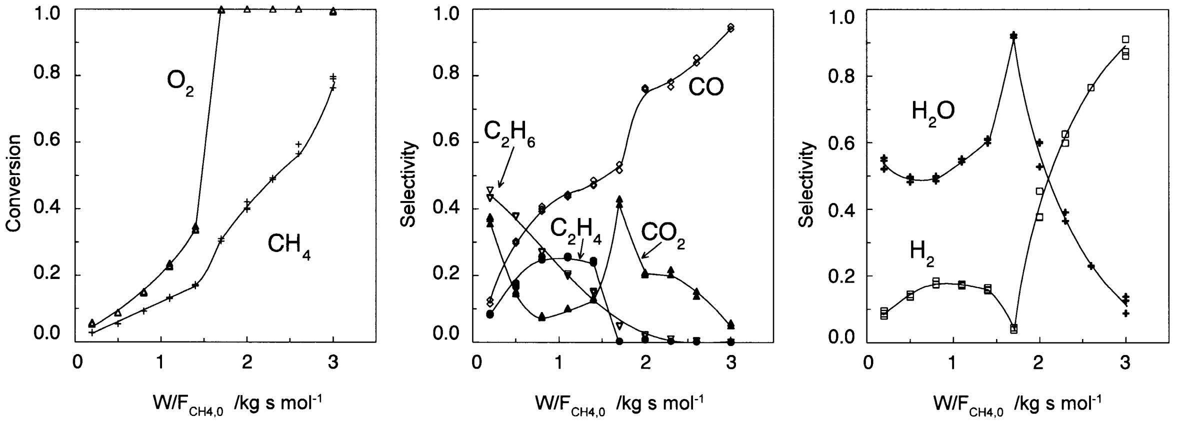

Fig. 3. Conversions and selectivities on Rh/α-Al_2O_3 as a function of the space time. $T = 1285$ K, $p = 400$ kPa, $CH_4/O_2/He|_0 = 6.7/3.3/90$.

tive conclusions can be drawn with respect to the reaction network. First the experiments in which He was used as a diluent are considered. Here, the occurrence of gas-phase chain reactions can be ruled out and the process can be treated as a classical set of heterogeneous reactions. Also Dietz III and Schmidt [18] found evidence that gas-phase reactions do not play a major role under conditions similar to those used here. However, it cannot be ruled out that some gas-phase reactions are initiated on the surface of the catalyst. For instance, coupling of CH_3 species, formed on the catalyst surface, can take place in the gas-phase, as is well accepted in work published on the oxidative coupling of methane [11].

Fig. 5 gives a schematic representation of the reaction network. The results clearly indicate that the primary products are CO_2, C_2H_6 and H_2O, and that CO and C_2H_4 are formed from these via consecutive reactions. Solymosi et al. [20] also observed the formation of C_2H_6 upon the adsorption of CH_4 on supported Rh catalysts, but in the absence of oxygen. When CH_3 radicals, formed on the catalyst surface, have coupled, C_2H_4 is most probably formed by oxidative dehydrogenation of ethane [19], as the curve for the selectivity of ethene increases to a maximum where the one for ethane continually decreases. At very low oxygen conversion, a high surface coverage by oxygen adatoms will probably be the cause of the complete oxidation to CO_2 rather than the formation of CO. For the same reason hydrogen adatoms, originating from dissociatively adsorbed CH_4 [12,20], will mainly react to form H_2O. Larger amounts of CO and H_2 are formed when the conversion of oxygen increases.

The observation that the addition of CO_2 or H_2O to the feed had no influence on the conversions and selectivities suggests that reforming reactions are not important at oxygen conversions lower than 100%. The presence of significant amounts of CO and H_2 at oxygen conversions lower than 100% then suggests that the direct formation of CO and H_2 from CH_4 and O_2 may also be possible and increasingly important at increasing oxygen conversion. This alternative route is drawn in the tentative reaction scheme of fig. 5. The present results cannot easily be explained by the reaction mechanism proposed by Buyevskaya et al. [12] in which CO is formed from carbon adatoms and CO_2 via a reverse Boudouard reaction on the catalyst surface.

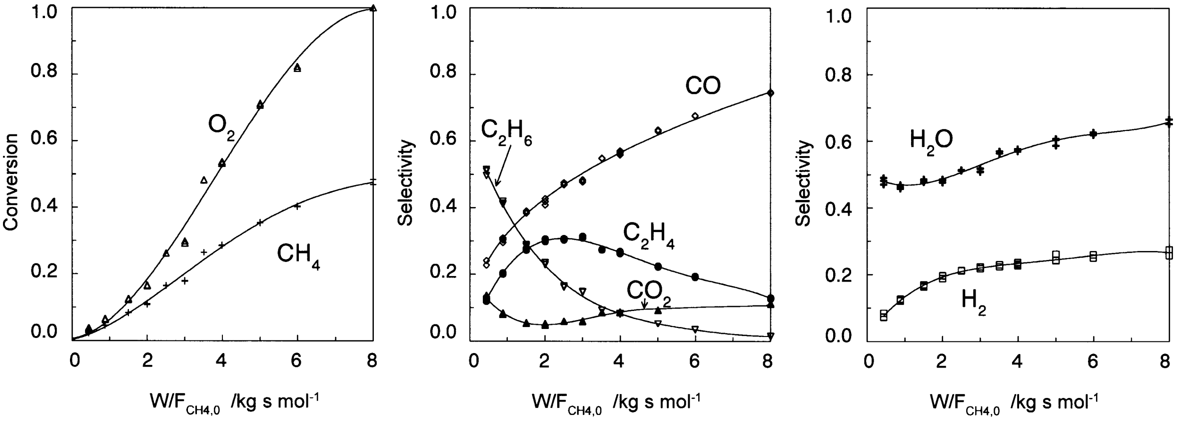

Fig. 4. Conversions and selectivities on the support as a function of the space time. $T = 1285$ K, $p = 400$ kPa, $CH_4/O_2/He|_0 = 6.7/3.3/90$.

Table 4
Experimental results without He dilution compared with results of the gas-phase model. Conditions: $T = 1060$ K, $CH_4/O_2 = 6.7/3.3$, 0.060 g support, 0.2781 g non-porous inert

	$p = 140$ kPa, $F_{tot} = 1.0 \times 10^{-4}$ mol s^{-1}		$p = 500$ kPa, $F_{tot} = 1.0 \times 10^{-3}$ mol s^{-1}	
	exp.	gas-phase sim.	exp.	gas-phase sim.
X_{CH_4}	0.02	0.08	0.09	0.10
X_{O_2}	0.05	0.14	0.21	0.26
$S_{C_2H_6}$	0.30	0.29	0.16	0.07
$S_{C_2H_4}$	0.10	0.36	0.11	0.16
$S_{C_2H_2}$	0.00	0.00	0.00	0.02
S_{CO}	0.43	0.28	0.64	0.66
S_{CO_2}	0.17	0.04	0.08	0.08
S_{H_2}	0.09	0.10	0.09	0.03
S_{H_2O}	0.63	0.58	0.73	0.83

According to Torniainen et al. [21], carbon may be formed on the catalyst surface at CH_4/O_2 ratios higher than 2.0. It would therefore be possible that at $CH_4/O_2 > 2.0$ carbon covers part of the catalyst surface and deactivates the catalyst, whereas at $CH_4/O_2 < 2.0$ the surface is clean and the catalyst exhibits a much higher activity. However, in the experiments from which the partial reaction orders of CH_4 and O_2 were determined, where the CH_4/O_2 ratio varied from 1.0 to 4.0, no drastic changes in the conversions and selectivities at a particular ratio were observed. Other experiments, performed at various CH_4/O_2 ratios in the range from 1.9 to 2.1, resulted in small variations of the conversions and selectivities which do not point to the formation or removal of a substantial amount of carbon at $CH_4/O_2 = 2.0$.

It was shown in our experiments that the support is not inert at 1285 K, but exhibits activity for oxidation reactions, both complete and partial. Even using the support alone, significant selectivities to ethane and CO were obtained. The support has low activity for reforming reactions when all oxygen has been consumed, but the behaviour in the presence of oxygen shows similarities with that of the catalyst. Although the conversions found with the support are lower than half of those observed with the catalyst, the trends in the selectivities are the same for both materials. This becomes more evident when the selectivities as a function of the oxygen conversion for the catalyst and the support are compared in figs. 6 and 7. At the lowest oxygen conversion measured, the selectivity to CO_2 found on Rh/α-Al_2O_3 was higher, and that to CO lower, than on the support alone, but at the other oxygen conversions the selectivities found on Rh/α-Al_2O_3 were very close to those found on the support alone. This similarity indicates that, at low oxygen conversions, the reactions occurring on the support are the same as on the rhodium. This could be explained by assuming that rhodium is in a partly oxidized state and that the Rh-oxide behaves similarly to the alumina. Mallens et al. [3] showed that, during steady-state experiments in a stoichiometric mixture, i.e. $CH_4/O_2 = 2$, the rhodium sponge had been oxidized, corresponding to ten theoretical monolayers, and that the amount of rhodium oxide increased with decreasing CH_4/O_2 ratios. Thus, under reaction conditions, at least part of the Rh can be present as an oxide. When the surface areas are taken into account, the turnover frequency (TOF) on Rh-oxide is about 10 times higher than that on alumina. Mallens et al. [3] and Buyevskaya et al. [12] showed that metallic Rh sites are available in the rhodium oxide and propose that these metallic Rh sites adsorb methane; this can explain why the 0.3% Rh/Al_2O_3 has a higher TOF than the alumina support alone.

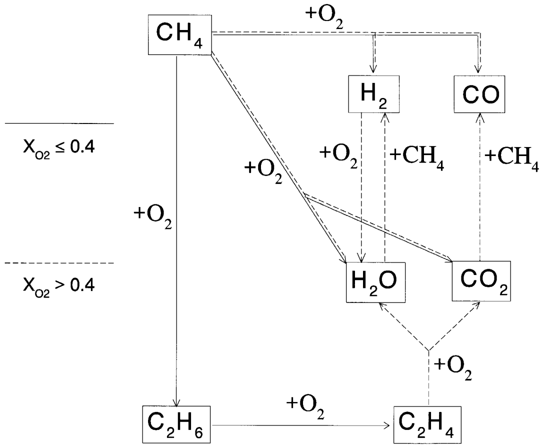

Fig. 5. Tentative schematic representation of the reaction network on Rh/α-Al_2O_3.

In the work described here, some observations were made which seem to contradict those of Mallens et al. [3], who studied Rh- sponge using TAP at low pressures (0.1 kPa) and temperatures up to 1023 K. Under those conditions, the influences of gas-phase reactions *and* of the support were excluded. Neither ethane nor ethene was observed, and CO and H_2 were found to be the predominant primary products. Since gas-phase reactions do not play an important role in the present experiments

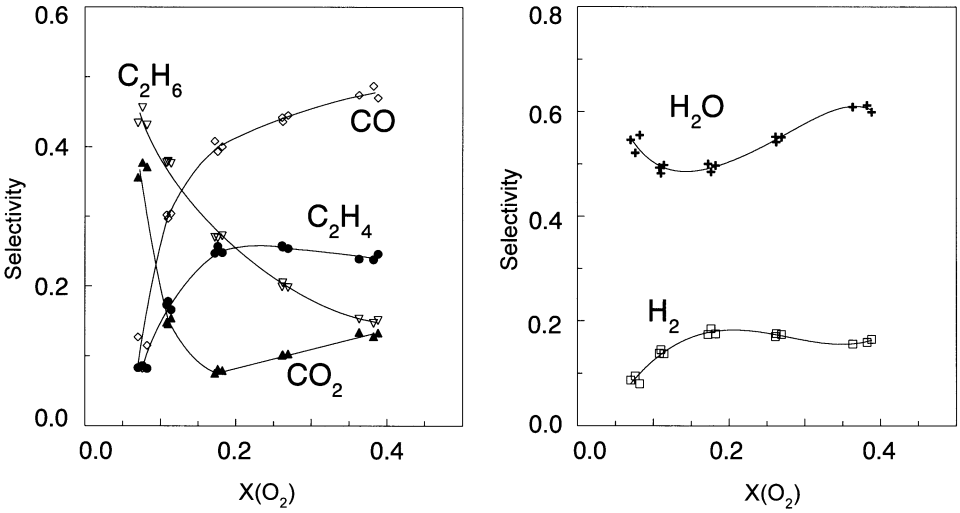

Fig. 6. Selectivities on $Rh/\alpha\text{-}Al_2O_3$ as a function of the oxygen conversion. $T = 1285$ K, $p = 400$ kPa, $CH_4/O_2/He|_0 = 6.7/3.3/90$.

either, the main source of the difference lies in the α-Al_2O_3 support. As was concluded from a TAP study by Heitnes et al. [22] using the same catalyst as in the present experiments, the α-Al_2O_3 support is expected to act as a reservoir of oxygen, which enhances the formation of CO_2 and H_2O rather than that of CO and H_2. Hickman et al. showed that the formation of OH groups on Rh is highly activated [1]. On alumina, OH groups are known to be present even at high temperatures [23]. Reverse spillover of OH to the rhodium surface may be the origin of the observation that at low oxygen conversions the selectivity to H_2O, formed from adsorbed OH, is always much higher than that to H_2, which is formed from hydrogen adatoms. Wang et al. [13] propose that adsorbed OH species play an important role in the formation of both H_2O and CO_2, which they found to be primary products at low oxygen conversion during TAP studies using a 0.05 wt% Rh/Al_2O_3 catalytst with a high BET surface area.

As yet, no explanation has been given for the steep increase of the conversion above $X_{O_2} = 0.4$. A similar change was reported in the previously mentioned TAP study by Heitnes et al. [22] using the same catalyst as the one used in the present experiments. The authors showed that in steady-state experiments the selectivity pattern changed suddenly from CO_2/H_2O to CO/H_2 after a certain time. Although there is no direct experimental evidence for this, there might be a complete reduction of the Rh-oxide at this point. This would be similar to results reported on nickel catalysts [6]. A change in oxidation state dependent on the environment in CO oxidation was also found by Kellogg [24] who described how a Rh-oxide field emitter at 500 K was instantaneously reduced above CO/O_2 ratios of 1/40. It seems therefore possible

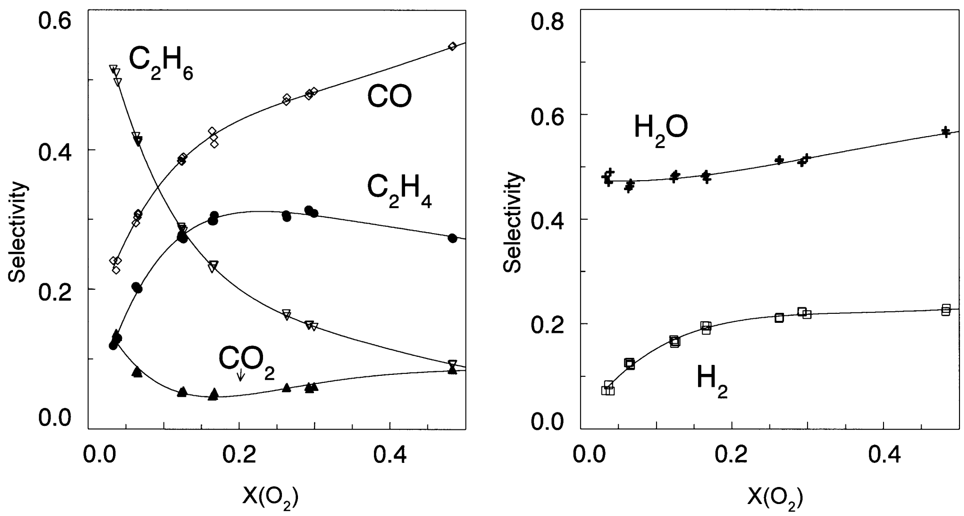

Fig. 7. Selectivities on the support as a function of the oxygen conversion. $T = 1285$ K, $p = 400$ kPa, $CH_4/O_2/He|_0 = 6.7/3.3/90$.

that in the experiments described here, at an oxygen conversion of 0.4, the gas mixture is capable of reducing the Rh-oxide completely. In the presence of oxygen, metallic rhodium is apparently very active for the oxidation of CH_4, C_2H_4 and H_2; also CO is expected to be oxidized, but its dissappearance is probably compensated for by its formation both in the oxidation of ethene and in the CO_2 reforming of methane.

When the oxygen conversion is complete, the remaining CH_4 is reformed with CO_2 and/or H_2O to CO and H_2, which is catalysed by metallic rhodium [9]. These reactions have been extensively reviewed in the literature [9,25–27].

In the absence of helium as a diluent, the partial pressures of methane and oxygen were 3–12 times higher than with helium. The gas-phase model shows that under these conditions gas-phase reactions may become important. However, at 140 kPa, where p_{CH_4} and p_{O_2} are three times higher than in the diluted case, the observed conversions are only about a third of those predicted by the gas-phase model. The gas-phase model, which is based on experiments in an empty reactor, does not account for wall effects, in particular termination of chains by collision of radicals with inert surfaces. In our experiments, however, the reactor was filled with support and non-porous alumina, which provides a small but significant surface area. This surface area appears to be able to quench radicals and thus inhibit part of the gas-phase reactions to take place. At 500 kPa, though, where p_{CH_4} and p_{O_2} are 12 times as high as in the diluted case, the wall effect is too low and consequently the gas-phase model compares very well with the experiments.

7. Conclusions

Under conditions close to those industrially relevant, the catalytic partial oxidation of methane can still be described in a classical way. Intrinsic kinetic data could be obtained, from which a reaction network was derived. This provides a useful basis for the simulation of reactor operation at a larger scale. The latter requires a reaction model describing the kinetic data quantitatively, both at low conversions, where the catalyst is probably in an oxidic state, and at higher oxygen conversions, where the catalyst is probably in a reduced state. In such a model the catalytic activity of the support has to be taken into account, as well as reverse spill-over of OH onto the metal and the surface initiated gas-phase formation of ethane and ethene. One step further, also gas-phase chain reactions, which become important at higher partial pressures, and heat effects will have to be included into the reaction model. In this context it is also important to note, that for practical application the formation of significant amounts of CO at low oxygen conversions is beneficial for the heat management of the reactor.

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