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Partial oxidation of methane to synthesis gas over rhodium catalysts

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Abstract

The partial oxidation of methane to synthesis gas has been studied using the temporal-analysis-of-product (TAP) set-up on different Rh catalysts. Rh sponge diluted with either SiC or α-Al_2O_3, and 0.3 wt% Rh/α-Al_2O_3 were investigated using pulses and continuous flow of methane and oxygen. The effect of introducing a support in the catalyst system was given special concern.

Blank experiments on the α-Al_2O_3 support showed no activity for the partial oxidation of methane in the 673–1123 K range. Oxygen multipulse experiments on the 0.3 wt% Rh/α-Al_2O_3 and on the pure support showed that α-Al_2O_3 is not inert concerning adsorption, desorption and storage of oxygen.

Totally oxidized catalysts show low activity because of few sites for methane dissociation. Mainly, total oxidation products CO_2 and H_2O are formed. The formation of these products partially reduces the catalyst whereupon with time-on-stream a steep discontinuity is observed in the methane and oxygen conversion as reduced metal sites largely increase the rate of methane dissociation. The discontinuity is followed by a continuous change in the product distribution from CO_2 and H_2O towards CO and H_2. The time-on-stream, before an active catalyst was obtained, increased with increasing amount of oxygen in the feed. The time before obtaining an active catalyst also depended on the catalyst system and changed in the following way: Rh sponge mixed with SiC<Rh sponge mixed with α-Al_2O_3<Rh/α-Al_2O_3. The latter indicates a spillover effect of oxygen from the support to the metal which also affects the steady-state methane conversion and syngas selectivity. The CO, CO_2 and H_2O pulse responses shifted to shorter times with increasing amount of oxygen in the feed, while H_2 showed the opposite effect. This indicates a faster formation of the products containing oxygen but sorption effects may not be excluded. Removal of surface oxygen by methane pulsing led to oxygen migration from the Rh bulk resupplying the surface.

When the catalyst is at steady state, CO and H_2 are formed as primary products on a Rh sponge mixed with SiC. Experiments on Rh sponge mixed with α-Al_2O_3 or a Rh/α-Al_2O_3 showed the same product sequence and unless sorption effects disguise the real primary product formation the sequence is not altered by the support. It is believed that the formation of primary products depends on the amount of oxygen available on the surface. © 1998 Elsevier Science B.V.

1. Introduction

The direct partial oxidation of methane to synthesis gas has obtained a renewed interest, during the last years. Commercially, steam reforming is the established process for converting natural gas into syngas [1]. Steam reforming in different combinations with partial combustion gives a highly efficient plant, but with large investment costs.

The catalytic partial oxidation of methane to syngas is not a new idea. Work on a nickel catalyst was reported already by Prettre et al. [2]. During the last

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years, a large number of research groups [3–24] have been searching for catalysts capable of producing syngas selectively at relatively low temperatures. Promising catalytic systems have been rhodium, platinum, ruthenium, palladium, iridium, cobalt and nickel on different supports. Work on catalytic partial oxidation has been reviewed by Foulds and Lapszewicz [25]. Most of these studies have reported an equilibrium product distribution, while Lapszewicz and Jiang [7,8] and Choudhary et al. [5,6] reported catalysts with CO yields higher than predicted at equilibrium. Considerable care should be taken when interpreting these results due to possible hot spots in the catalyst bed [25–27].

No final agreement on the reaction mechanism has yet been obtained. One possibility is that part of the methane is completely oxidized to CO_2 and H_2O followed by reforming reactions converting the remainder of the methane to syngas [2–4,9–12,14–17,21]. Hickman and Schmidt [28,29] claim that CO and H_2 are formed directly as primary products on Pt and Rh impregnated monoliths and on Pt/10% Rh metal gauzes at high temperatures and short residence times of 10^{-2}–10^{-4} s. The experimental work is supported by a reaction model consisting of 19 elementary reaction steps [30]. Lapszewicz et al. [7,8] reported, by studying different catalysts at different space velocities, that both CO, CO_2, H_2 and H_2O could be primary products.

Recently, Buyevskaya et al. [31] studied the partial oxidation on a 1 wt% Rh/γ-Al_2O_3 by applying the temporal-analysis-of-product (TAP) set-up. It was found that the product distribution was strongly affected by the degree of surface reduction. Carbon species and CO_2 were primary products, while CO was formed from the reverse Boudouard reaction. In a recent paper [32], the same group studied Rh-sponge catalysts giving similar conclusions concerning primary products. Mallens et al. [33,34] studied the partial oxidation of methane on Pt- and Rh-sponge catalysts. Methane was found to decompose on reduced metal giving surface carbon and hydrogen. For the Pt sponge CO and CO_2 were formed in parallel by involvement of different oxygen species. At a stoichiometric feed ratio the dominant reaction pathway was the direct formation of CO and H_2 followed by their consecutive oxidation. The Rh catalyst contains two different forms of oxygen. CO is formed from surface carbon and oxygen present as rhodium oxide, while the consecutive oxidation of CO and H_2 proceeds via both chemisorbed oxygen and rhodium oxide. A Mars–van Krevelen redox cycle was postulated for both systems where methane reduces the metal oxide which is reoxidized by oxygen from the feed. Recently, Slaa et al. [35,36] found that CO_2, C_2H_6 and H_2O are primary products on a 0.3 wt% Rh/α-Al_2O_3 catalyst, and that CO and C_2H_4 are formed from these via consecutive reactions.

The results discussed above show that different conclusions have been drawn with respect to the primary products. One observation among the authors claiming to have an isothermal catalyst bed [21,31,33–36], which is essential for the determination of primary products, is that CO and H_2 seems to be primary products on pure metals, while CO_2 and H_2O are primary products in catalytic systems containing a carrier. Further investigations on the effects of introducing a carrier to the catalytic system were found essential.

2. Experimental

2.1. Catalysts

The supported Rh catalyst was 0.3 wt% Rh/α-Al_2O_3 made by impregnating a low surface area α-Al_2O_3 support with a solution of $Rh(NO_3)_3\cdot 2H_2O$. The impregnated catalyst was dried at 373 K, heated at 473 K in nitrogen and reduced at 530 K in hydrogen. The Rh surface area, which was found by CO adsorption and by assuming a CO/Rh activity of 1, was 0.019 m^2/g; and the pellet size 80–106 μm. The BET surface area of the α-Al_2O_3 was 0.12 m^2/g and the pore diameters were larger than 3 μm. Thereafter, 0.375 g 0.3 wt% Rh/α-Al_2O_3 was charged to the reactor. The low-surface area α-Al_2O_3 was supplied by Johnson Matthey, washed with nitric acid and, subsequently, heated at 1123 K. The support contained only very small amounts of impurities after the treatment.

The Rh catalyst used was Rh sponge (99.9% from Johnson Matthey) with a pellet size of 0.25–0.35 mm. The BET surface area was 0.25 m^2/g for the fresh catalyst and 0.19 m^2/g after pretreatment. Thereafter, 0.0375 g of the Rh sponge, which gives the same amount of exposed Rh as 0.375 g Rh/α-Al_2O_3, was charged to the reactor. This catalyst was physically mixed with 0.375 g of the pure α-Al_2O_3 (the same as used for the impregnated catalyst) or with 0.375 g SiC with a pellet size of 80–106 μm. The SiC pellets had a BET surface area of 0.24 m^2/g and were non-porous. Elemental analysis of the SiC showed only very small impurities of Al, Fe, K, and Na. A non-porous α-Al_2O_3 (1.56 g) or the SiC (1.20 g) with a 150–212 μm pellet size was used as an inert packing material.

Prior to the experiments, the Rh sponge, the 0.3 wt% Rh/α-Al_2O_3 and the pure α-Al_2O_3 were pretreated for 1 h in flowing oxygen and 1 h in flowing hydrogen at 1273 K. This was done in order to prevent rhodium from sintering during experiments at high temperatures and to remove impurities of C, P and S.

2.2. TAP–reactor system

A TAP set-up described in Ref. [37] was used for the experimental work. TAP is a transient response technique which allows transient experiments to be carried out on a millisecond time scale. The experiments are performed by introducing a narrow gas pulse into the reactor containing the catalyst, and continuously evacuating at the reactor outlet. The transient responses of reactants and products are measured with a quadropole mass spectrometer. The pulse size may be chosen very small (10^{13}–10^{16} molecules per pulse) in order to limit the number of gas molecules compared to the number of exposed catalyst sites. In this way, the catalyst may be studied at a well-defined state of the surface. The shape of a response is influenced by the different processes taking place, like diffusion, adsorption, desorption and reaction. Comparison of the different reactant and product responses gives information on the reaction network.

Different types of experiments may be performed with the TAP apparatus. In this work, the continuous-flow mode was used for catalyst pretreatment and for obtaining a steady-state coverage on the catalyst surface. The quadropole is then working in a scan mode, scanning a preset mass range. Two different types of transient experiments were performed: pulse experiments and multipulse experiments. In the first method, the response to a single pulse is measured at a fixed atomic mass unit, and several pulses are averaged to improve the signal-to-noise ratio. In the multipulse experiments a series of pulses are introduced, and the responses of all pulses are measured separately at a fixed atomic mass unit, without signal averaging. In all pulse experiments smoothing of the curves was applied.

The Inconel microreactor was filled with the impregnated Rh catalyst or with Rh sponge diluted with α-Al_2O_3 or SiC. The catalyst bed was 12 mm long or less to ensure isothermal operation. Two thermocouples were inserted inside the catalyst bed and the axial temperature difference was always lower than 10 K. The microreactor had a length of 42 mm and an inner diameter of 6 mm. The reactor was packed with non-porous α-Al_2O_3 or SiC at each end of the bed.

The reaction products were CO, CO_2, H_2 and H_2O, while no formation of higher hydrocarbons were observed. Thereafter, 10–15% of argon was added as an internal standard in the pulse experiments to calculate the amount of reactants and the conversion. Corrections were made for the contribution of CO_2 to the mass 28 signal. In the pulse experiments, unless otherwise mentioned, the ratio between admitted reactant CH_4 molecules and the number of exposed Rh sites was chosen to be ca. 0.05 by using inlet pulses of $\approx 5\times 10^{15}$ molecules. By using these small reactant pulses gas-phase reactions could be neglected.

3. Results and discussion

3.1. Oxygen uptake on a 0.3 wt% Rh/α-Al_2O_3 catalyst

The oxygen uptake was investigated on the 0.3 wt% Rh/α-Al_2O_3 in the 673–1123 K range. The catalyst was completely reduced with a continuous flow of hydrogen, and multipulses of oxygen were then applied to measure the oxygen uptake. At 1123 K, the O_2 uptake was more than three times larger than a theoretical uptake corresponding to a complete oxidation of the Rh bulk to Rh_2O_3. This shows that the α-Al_2O_3 support is able to take up oxygen possibly by adsorption to surface OH-groups. It is not likely that α-Al_2O_3 can be reduced in hydrogen. The O_2 uptake also increases steeply with increasing temperature. At 1123 K, the O_2 uptake is 35 times higher than at 673 K. The oxygen uptake on the α-Al_2O_3 in the

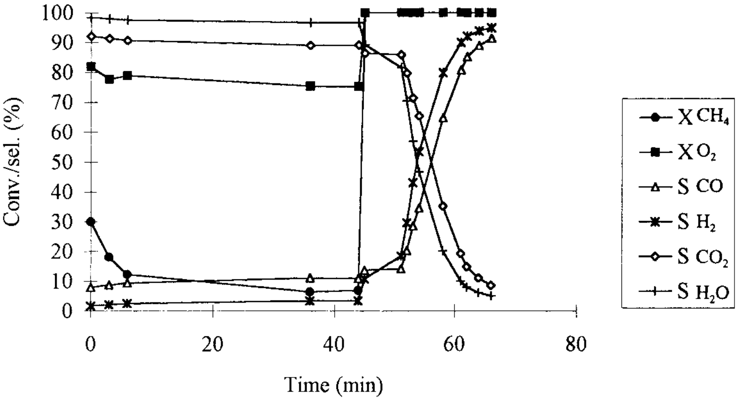

Fig. 1. Conversions (*X*) and selectivities (*S*) as a function of time-on-stream over Rh sponge diluted with α-Al_2O_3 (1 : 10) pretreated in O_2. Continuous feed $CH_4/O_2=2$, $T=1123$ K.

Rh/α-Al_2O_3 catalyst was verified by experiments using the pure support.

The desorption of oxygen was measured by multipulsing of oxygen after exposure of the oxidized catalyst to vacuum during different time intervals (10, 5, 2 and 0.5 min) at 1023 K giving a linear increase in desorption with increasing time. After 10 min, the amount corresponded to 2.2 monolayers. Desorption from the α-Al_2O_3 was verified by measuring O_2 uptake on the pure support.

These experiments clearly indicate that even an α-Al_2O_3 support is not inert concerning adsorption and desorption of oxygen. It should be noted that the support was already tested for the partial oxidation of methane in the 673–1123 K range showing no activity.

3.2. Interaction of continuous feeds of different CH_4/O_2-ratios with a fully oxidized Rh sponge

Rh sponge was diluted with pure α-Al_2O_3 in the 1 : 10 ratio. This physical mixture was loaded into the reactor and heated to 1023 K in vacuum. At 1073 K, the catalyst was exposed to a continuous flow of O_2/Ar for 120 min giving a completely oxidized Rh metal as no further oxygen uptake was observed. Mallens et al. [34] showed by thermodynamic calculations that the Rh_2O_3 phase is stable at an oxygen pressure of 250 Pa or higher, which is the same order of magnitude as in the TAP experiments. The system was exposed to vacuum for 15 min, and then a continuous flow of methane and oxygen at a total flow rate of 2×10^{-7} mol/s at different ratios was fed over the catalyst bed as shown in Figs. 1–3.

Using the stoichiometric ratio between methane and oxygen for syngas production, the completely oxidized catalyst is not very active as shown in Fig. 1. The initial conversion of methane is 30% which decreases to ca. 10% within the first 10 min. The oxygen conversion is close to 80%, and it should be noted that the oxygen balance is not closed, with excess oxygen leaving the system. The main products are the total oxidation products, CO_2 and H_2O, with more than 90% selectivity. The formation of CO_2 and H_2O decreases slightly with increasing time-on-stream until ca. 45 min, when the conversion of both methane and oxygen increases to 100% and the product distribution starts changing from CO_2 and H_2O towards CO and H_2. The selectivity of CO and H_2 attains values of more than 90%, 20 min after the sudden increase in conversions.

The CH_4/O_2 ratio was increased to 3 and the same experiment as described above was performed to study the influence of the feed ratio on the course of the reaction on the initially oxidized catalyst. These results are given in Fig. 2. The initial methane conversion is 24% decreasing below 10% within the first 5 min. The selectivity to CO_2 and H_2O is initially above 90%. Then only after 14 min on stream, the methane and oxygen conversion suddenly reaches 100%, showing the same behavior as in the previous experiment. Conditions near steady state was reached

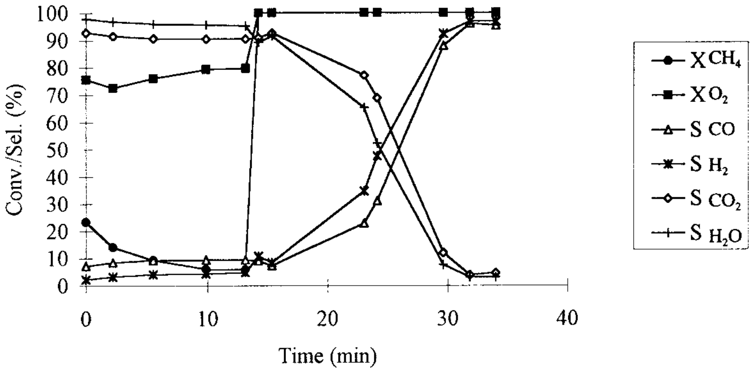

Fig. 2. Conversions (*X*) and selectivities (*S*) as a function of time-on-stream over Rh sponge diluted with α-Al_2O_3 (1 : 10) pretreated in O_2. Continuous feed CH_4/O_2=3, *T*=1123 K.

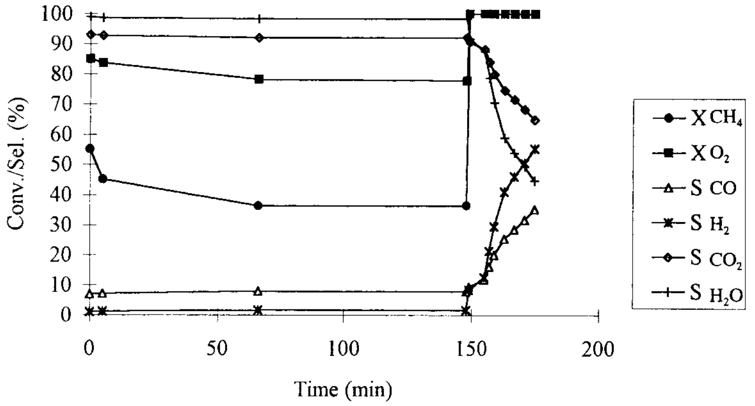

Fig. 3. Conversions (*X*) and selectivities (*S*) as a function of time-on-stream over Rh sponge diluted with α-Al_2O_3 (1 : 10) pretreated in O_2. Continuous feed CH_4/O_2=1, *T*=1123 K.

after 33 min giving more than 95% selectivity to CO and H_2.

A H_4/O_2 ratio of 1 was also tested as shown in Fig. 3. In this case, the initial methane conversion was quite high, 56%, slowly decreasing to 38% within 145 min. After 145 min, a methane and oxygen conversion of 100% was still not obtained and some small amounts of pure methane were pulsed over the catalyst. Each methane pulse contained ca. 4.5×10^{15} molecules, the total amount pulsed being 2.2×10^{17}. As soon as the CH_4/O_2 mixture was switched back, the methane conversion was 100%. After the discontinuity the same behavior was seen as in the two other experiments, the product distribution changed from CO_2 and H_2O towards CO and H_2. With a CH_4/O_2 ratio of 1 a hydrogen selectivity of 55% and a CO selectivity of 35% was reached, but it still continued to increase even after the experiment was terminated.

It is obvious from these experiments that a completely oxidized catalyst is not the optimum state for the partial oxidation of methane to synthesis gas, probably because of a low ability for CH_4 dissociation. The more oxygen in the feed the more time is required to obtain complete conversions of methane and oxygen on the preoxidized catalyst. The steep increase in conversion is believed to occur, when some of the metal oxide is reduced to metal allowing methane to dissociate more readily on the surface. During the initial period, some small amounts of methane are converted to CO_2 and H_2O with their formation causing a reduction of the Rh oxide to Rh metal. The more oxygen in the feed the more time is required to reduce the metal since more oxygen is supplied from the gas phase.

The interaction of methane and oxygen with partial oxidation catalysts has been studied recently by several groups. Slaa et al. [35,36] found a steep increase in the oxygen conversion by increasing the space time using the same catalyst as in the present experiments. After the steep increase, at even longer space times, the product distribution changed from CO_2 and H_2O towards CO and H_2. The authors suggest that there might be a complete reduction of the Rh oxide at this point. Mallens et al. [34] found by alternating pulse experiments, varying the time interval between pulses of methane and oxygen, that short-living chemisorbed oxygen was involved in the non-selective oxidation of methane. Buyevskaya et al. [31,32] observed that the product distribution is strongly dependent on the degree of surface reduction on a 0.1 wt% Rh/γ-Al_2O_3. Mallens et al. [34] and Buyevskaya et al. [31,32] found methane dissociation to occur on reduced surface sites. Au et al. [38] studied methane and oxygen interactions on Ni/SiO_2 by pulse experiments. They found lattice oxygen in NiO to be responsible for complete oxidation, while syngas could be formed only on reduced nickel. Hu et al. [39] studied partial oxidation of methane on Ni/La_2O_3 and concluded that the CO selectivity largely depends on the strength of oxygen species bonded to the catalyst, and that a reduced catalyst is more active than an oxidized catalyst for the dissociation of methane. Burch and Loader [40] examined methane oxidation on a Pt/Al_2O_3 catalyst under transient reaction conditions. An intermediate surface with respect to adsorbed methane and oxygen was required to obtain optimum reactivity. Burch and Hayes [41] found that the optimum state for the activation of C–H bonds in CH_4 corresponds to a partially oxidized Pt surface. Recently, Qin et al. [42] concluded that the rate of CO vs. CO_2 formation is strongly dependent on the oxygen–metal bond strength.

The sudden change in reaction rates has been observed previously by several authors [4–7], but always as a function of temperature. The actual temperature depends on the catalyst used and on the partial pressures of the reactants. Dissanayake et al. [4] and Choudhary et al. [5,6] found the threshold temperature to be dependent on the catalyst pretreatment. An oxidized catalyst had a relatively high threshold temperature. A partially reduced catalyst, obtained by exposure to reaction conditions at high temperatures, lowered this critical temperature. These results fit well with the observations in this work, at a constant temperature, but at a changing oxidation state.

The relatively high initial conversion of methane is not easily explained. The vacuum pretreatment removes some weakly adsorbed oxygen which might give a larger possibility for methane to adsorb. The surface will soon be reloaded again by the continuous methane/oxygen mixture and the methane conversion will continue to decrease. However, there is still a low conversion of methane consuming oxygen and reducing the catalyst. As already mentioned, the time required for obtaining complete conversion is longer when the more oxygen is fed. This happens despite the fact that the initial methane conversion is higher when the more oxygen is fed. It means that the supply of oxygen from the gas phase is larger than the reducing effect given by a larger methane conversion.

It is interesting to compare the product distribution near steady state with equilibrium calculations (Table 1). The system can be described by total combustion, steam reforming and the water–gas shift reaction while carbon formation is not included in the calculations. For the CH_4/O_2 feed ratio of 2, the equilibrium calculations give complete conversion of methane and 100% selectivity to synthesis gas. The experimental selectivities to CO and H_2 are 91 and 95%, respectively, in other words not far from equili-

Table 1
Experimental values for the partial oxidation of methane over the Rh sponge mixed with α-Al_2O_3 and equilibrium calculations of conversions and selectivities at different CH_4/O_2 feed ratios. Temperature T=1123 K, P=100 Pa

Conv./Sel. (%)	CH_4/O_2=2		CH_4/O_2=3		CH_4/O_2=1	
	Exp.	Equil.	Exp.	Equil.	Exp.	Equil.
X CH_4	100	100	100	67	100	100
X O_2	100	100	100	100	100	96
S CO	91	100	95	100	35	65
S CO_2	9	0	5	0	65	35
S H_2	95	100	97	100	55	71
S H_2O	5	0	3	0	45	29

brium. At the highest CH_4/O_2 ratio the methane conversion is higher than predicted by equilibrium calculations, while the CO and H_2 selectivities are ca. 100%. This can be achieved by having another oxygen source available, e.g. oxygen adsorbed on the catalyst. This might also explain the product distribution at a CH_4/O_2 ratio of 1, which was quite far from equilibrium and at the same time producing more of the total oxidation products. However, it must be added that in the last experiment a steady-state condition was not obtained before the experiment was terminated. From the carbon, hydrogen and oxygen balances it was found that carbon and hydrogen were within the acceptable error limits of 15%, while the oxygen balance always showed excess oxygen leaving the system. It should be noted that the continuous flow experiments are transient as long as the oxidation state of the catalyst is not steady.

After reaching the pseudo steady state, pure methane was pulsed over the catalyst while the responses of the different products were detected. In Figs. 4 and 5 the CO and H_2 responses on methane pulsing after pretreatment at the different CH_4/O_2 ratios are shown. The CO responses (Fig. 4) show that the initial parts of the curves are different, with a faster response when the more oxygen is fed. By looking at the H_2 responses in Fig. 5 the opposite effect is seen, with a longer delay time for the lowest CH_4/O_2 ratio. For both CO_2 and H_2O responses (not shown), the effect was similar as that of the CO responses. All products containing oxygen have a shorter delay time with more oxygen in the feed, while H_2 shows the opposite behavior. This may indicate that there are enough Rh^0 surface sites for all the three feeds to convert methane completely after a steady state has been reached. However, with a lower CH_4/O_2 ratio more oxygen is available, making the oxidation reactions faster. It is possible that the effects described above may be coupled to stronger or weaker adsorption and desorption characteristics on the surfaces at different oxidation states.

After pulsing a total amount of 5.5×10^{18} CH_4 molecules over the catalyst, the $CH_4/O_2=2$ mixture was switched back to a continuous flow similar to that before the methane pulses. It was not possible to reload the catalyst with oxygen using the feed with

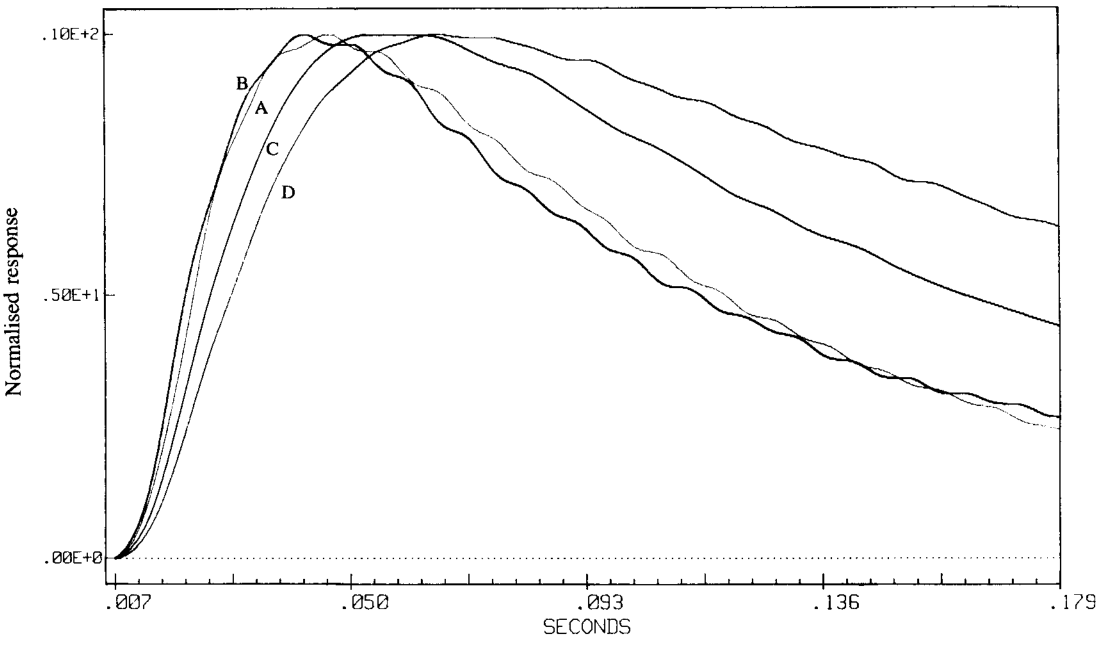

Fig. 4. Normalized CO responses on CH_4 pulsing after steady state is reached on the Rh sponge diluted with α-Al_2O_3 by a continuous CH_4/O_2 feed at different ratios. A, Ar response; B, $CH_4/O_2=1$; C, $CH_4/O_2=2$; and D, $CH_4/O_2=3$.

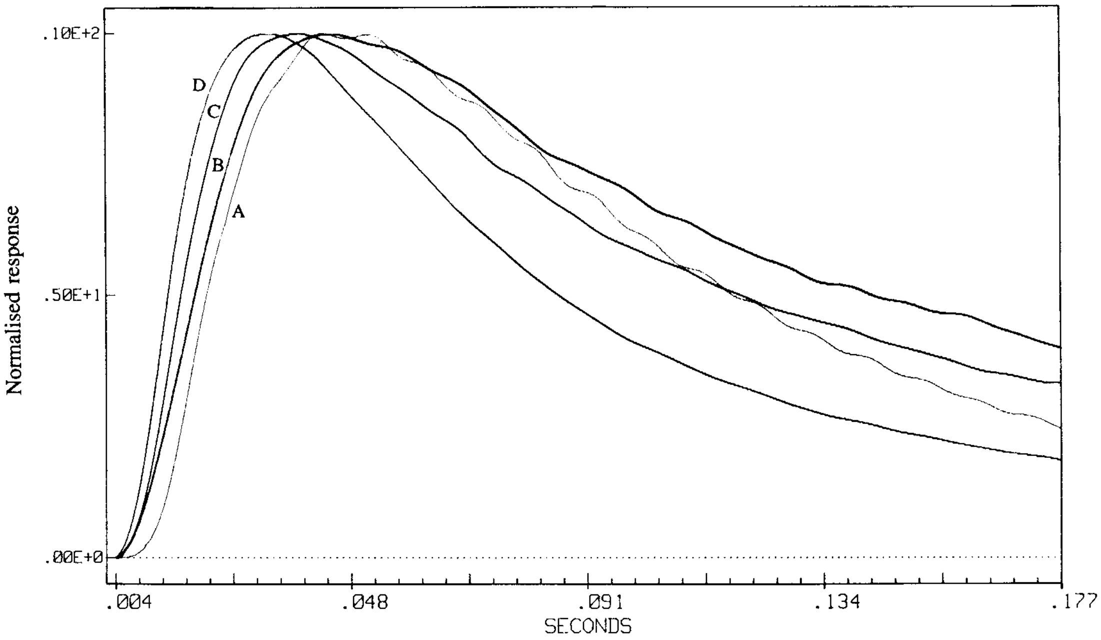

Fig. 5. Normalized H_2 responses on CH_4 pulsing after steady state is reached on the Rh sponge diluted with α-Al_2O_3 by a continuous CH_4/O_2 feed at different ratios. A, Ar response; B, CH_4/O_2=1; C, CH_4/O_2=2; and D, CH_4/O_2=3.

a CH_4/O_2 ratio of 2. The product distribution still showed mainly CO and H_2 as products, but methane was breaking through showing a decreasing methane conversion with increasing time-on-stream. Simultaneously, the amount of CO_2 increased at the expense of CO indicating that oxygen from the gas phase was reacting with surface carbon species forming CO_2. After 10 min, the feed was switched to pure oxygen. Initially no oxygen was found to leave the system, because it was incorporated into the catalyst. After 3 min on stream, which corresponds to an amount of 3.2×10^{20} oxygen molecules, oxygen was breaking through and the oxygen signal was still increasing after 20 min time-on-stream.

Several large methane pulses over a partly reduced catalyst resulted in methane breakthrough. After maintaining the catalyst at vacuum conditions, at different time intervals after the methane saturation, followed by exposure to small methane pulses, the result was a change in CO_2 formation. These results are shown in Table 2. By increasing the time interval from 90 to 1100 s, the amount of CO_2 increased with 40%. This shows migration of oxygen from the Rh bulk resupplying the surface.

Table 2
Number of moles of CO_2 formed by methane pulsing on the CH_4 saturated Rh sponge mixed with α-Al_2O_3 after exposure to different time intervals at vacuum

Time (s)	90	210	500	1100
CO_2 (mol)	3.4×10^{-10}	3.9×10^{-10}	5.5×10^{-10}	5.7×10^{-10}

3.3. *Comparison of different Rh-support combinations*

Results from the oxygen multipulse experiments on the 0.3 wt% Rh/α-Al_2O_3 catalyst and the pure α-alumina support showed a non-inert support with respect to adsorption, desorption and storing capacity of oxygen. The previous results on the Rh sponge mixed with α-alumina support showed that oxygen from the gas phase was reoxidizing the metal. This made it interesting to look into the effect of using a non-oxidic support to deduce if some oxygen in the above experiments was supplied from the α-alumina support.

SiC was chosen as the non-oxidic support and the Rh sponge was diluted ten times with SiC particles of

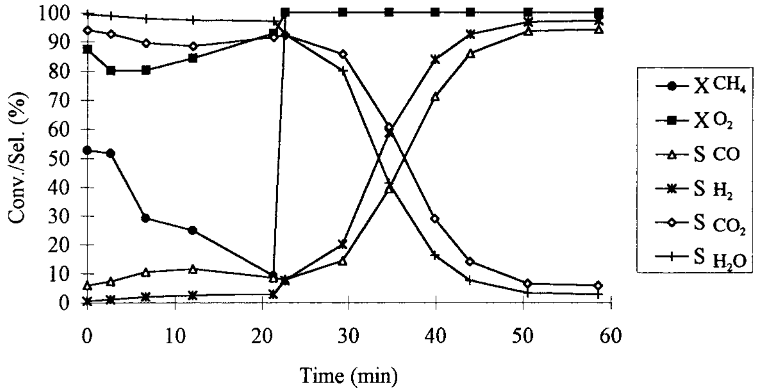

Fig. 6. Conversions (X) and selectivities (S) as a function of time-on-stream over Rh sponge diluted with SiC (1 : 10) pretreated in O_2. Continuous feed $CH_4/O_2=2$, $T=1123$ K.

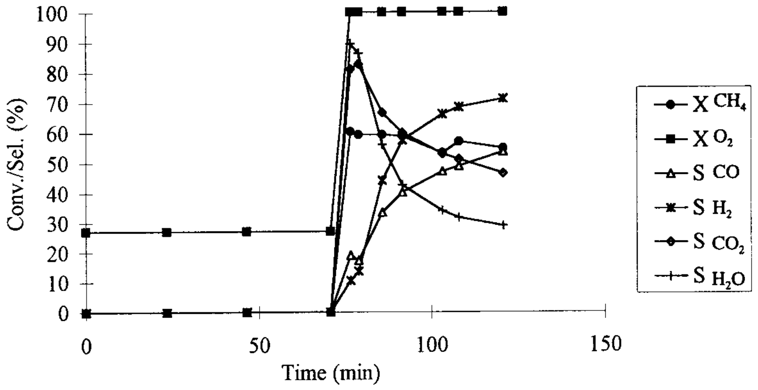

Fig. 7. Conversions (X) and selectivities (S) as a function of time-on-stream over 0.3 wt% Rh/α-Al_2O_3 pretreated in O_2. Continuous feed $CH_4/O_2=2$, $T=1123$ K.

the same size (80–160 μm) as the α-alumina support. The system was oxidized in flowing oxygen for 2 h at 1023 K, evacuated for 15 min with a continuous flow of methane and oxygen, at a ratio of 2 : 1, at the same flow rate as in the previous experiments was then fed. The conversions and product selectivities as a function of time-on-stream are given in Fig. 6, showing the same behavior as for the Rh sponge mixed with α-alumina support. Initially, a high methane conversion is found, which decreases slowly giving mainly the total oxidation products. A sudden increase in the conversion then appears, followed by a gradual change in the product distribution towards CO and H_2. The apparent steady state gives methane and oxygen conversions of 100% with syngas selectivity larger than 90%. This system shows the discontinuity after 21 min on stream compared to 45 min for the Rh sponge mixed with α-alumina at the same feed ratio. This is a clear indication that oxygen spilts over from the support to the metal in the case of the α-alumina support. The SiC does not provide a large resource of oxygen and, therefore, the reduction of the rhodium oxide will be faster.

The supported catalyst consisting of 0.3 wt% Rh/α-Al_2O_3 was also studied in the same way as described above and the results are given in Fig. 7. This system has a stronger interaction between the metal and the support and the spillover effect was believed to be stronger than that for the physical mixture. The initial methane conversion was zero and no increase could be observed within the first 70 min of operation. Probably as no methane conversion occurred, the metal was not reduced, leading to no increase in the methane conversion. However, some oxygen are converted, probably adsorbed on the catalyst. To initiate the methane conversion some pure methane was pulsed to the system. After pulsing 2×10^{17} methane molecules the feed was switched back to the continuous CH_4/O_2 feed. This treatment gave an active catalyst with a methane conversion of ca. 60% and a total oxygen conversion. The product distribution changed with increasing time-on-stream from the total oxidation products to synthesis gas. After a total time-on-stream of 120 min the CO and H_2 selectivities were 54 and 71%, respectively, and still continued to increase.

The Rh sponge mixed with α-alumina and the Rh sponge mixed with SiC gave almost the same product distribution near steady state. This is not the case with the supported catalyst. As shown in Fig. 7, the syngas selectivity is still slowly increasing, even 50 min after the discontinuity. The reverse spillover of oxygen may be more pronounced for the supported catalyst, with a closer contact between the metal and the support. The effect is that a longer time is needed to obtain CO and H_2. The CO selectivity is increasing very slowly on the supported catalyst in comparison with the other two catalytic systems. This effect may also be coupled to the methane conversion which is lower on the supported catalyst. The H_2 selectivity is increasing faster than the CO selectivity in all experiments, indicating that further oxidation of CO is easier than oxidation of H_2. This could also be due to a fast H_2 desorption or a strong CO adsorption. The effect can be seen in relation to the results discussed in Section 3.1 for the pulse experiments, where H_2 responses are moved to shorter delay times when less oxygen is present on the surface.

Little work has been done to identify the effect of the support in partial oxidation of methane to synthesis gas. Vermeiren et al. [3] tested the activity of Ni impregnated on different supports. The support was found to have little influence at a metal loading of 5%, but lowering the loading to 1% showed that the acidic supports gave lower conversions while the more basic supports showed unaltered conversions. A similar effect was reported by Choudhary et al. [5,6] who found the discontinuity temperature to be dependent on the support. The critical temperature was higher for acidic supports and lower for the more basic supports. Efstathiou et al. [43] tested Rh impregnated on different supports for the CO_2 reforming of methane. The most acidic supports showed the highest initial activity. The dependence of the activity to the metal particle size could be related to metal–support interactions, and the support also played an important role on the rate of deactivation. By studying mechanistic aspects it was found that a large reservoir of lattice oxygen species existed on a Rh/YSZ catalyst, while this was not the case for $Rh/\alpha\text{-}Al_2O_3$. Recently, Wang et al. [44] studied methane oxidation on a $Rh/\alpha\text{-}Al_2O_3$ catalyst. It was found that water adsorbed on the support acts as an oxygen source through the reverse spillover of water or hydroxyl onto the Rh particles.

The results from the present work support the theory that the support is not inert but acts as an additional source of oxygen. Since the ratio between the total oxidation products and synthesis gas formation depends on the amount of oxygen available, the support will provide extra oxygen and may as a result promote the production of the total oxidation products.

3.4. *Product sequences on the different catalysts*

Comparison of pulse response curves of the different products gives information on the reaction network. The starting point, rise time, peak maximum and the decay of the curve are determined by the different processes occurring in the system such as diffusion, adsorption, desorption and reaction. The gas transport in the system takes place mainly as Knudsen diffusion due to the low amount of reactant molecules. If the shape of the responses is only determined by Knudsen diffusion CO will be observed prior to CO_2 and H_2 prior to H_2O due to the difference in molecular weight. By calculating the Knudsen diffusion coefficients and by using adsorption and desorption rate coefficients from Hickman and Schmidt [30], Mallens et al. [34] simulated the response curves for pure Rh sponge. These simulations showed, by considering both Knudsen diffusion, adsorption and desorption, a shift in the sequences giving CO_2 prior to CO and H_2O prior to H_2.

In this work, the product sequences were studied by pulsing methane over the catalyst while measuring response curves, after steady state was obtained by a continuous flow of reactants at a CH_4/O_2 ratio of 2. The argon response and the different product responses for the Rh sponge diluted with SiC are

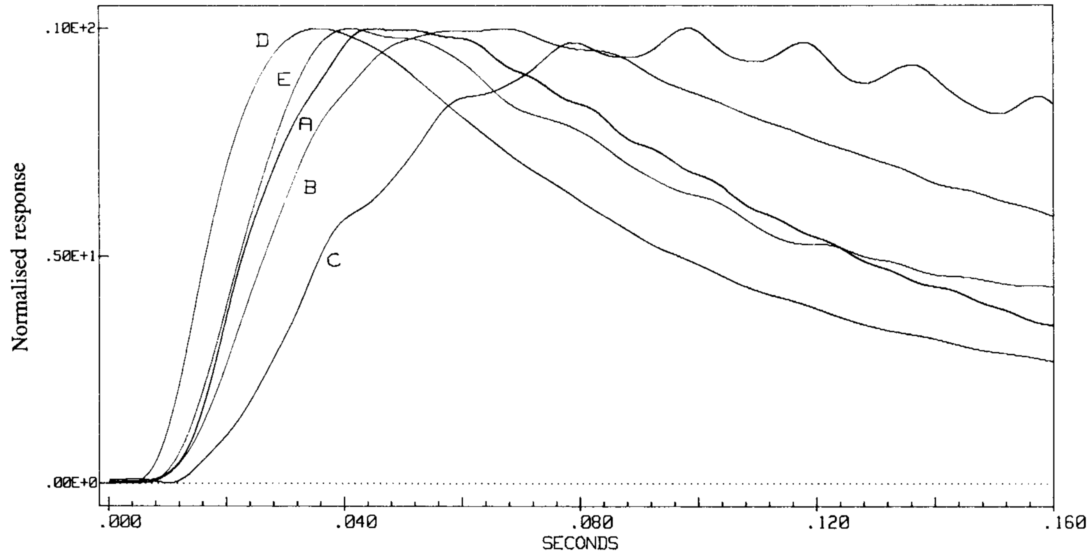

Fig. 8. Normalized responses on CH_4 pulsing over a Rh sponge diluted with SiC (1 : 10) at steady state after CH_4/O_2=2 pretreatment. A, Ar; B, CO; C, CO_2; D, H_2; and E, H_2O.

given in Fig. 8. The starting point and the peak maximum of CO are observed prior to CO_2, and the starting point and the peak maximum for H_2 is observed prior to H_2O. This is in accordance with the previous experiments by Mallens et al. [34] over pure Rh sponge and shows that CO and H_2 are primary products and that no large effects are observed by introducing a SiC support.

Similar experiments were performed on the Rh sponge diluted with the oxidic carrier α-Al_2O_3 (Fig. 9). By comparing Figs. 8 and 9, the main difference is found in the H_2O response. The starting point comes very early while the rise time is much delayed. The early start might be caused by some small amounts of H_2O continuously desorbing from the α-Al_2O_3. The delay is probably caused by water adsorbing more thoroughly on the α-Al_2O_3 than on the SiC. By comparing the hydrogen signal to the inert argon signal in each experiment, H_2 appears earlier from the SiC support. The starting points and responses of CO and CO_2 are similar for the two systems. Substituting the non-oxidic SiC with α-Al_2O_3 results in no large effects provided that steady state is achieved.

The responses on the 0.3 wt% Rh/α-Al_2O_3 gave the same product sequence as the Rh sponge diluted with α-Al_2O_3. The rise time of H_2O is even more delayed in this system. It is, however, difficult to distinguish between primary and secondary products in this system. The simulations using rate data taken from Hickman and Schmidt [30], are no longer valid since these data were found on pure metal surfaces. From the present experiments, it looks as if the product formation sequence is equal for Rh sponge mixed with SiC or α-Al_2O_3 and for supported rhodium. Care must be taken because sorption effects, which could possibly mask the real primary product formation, cannot be excluded.

The 0.3 wt% Rh/α-Al_2O_3 brought to an apparent steady state with a CH_4/O_2 mixture of 2 : 1 was also exposed to a pulse experiment at the same CH_4/O_2 ratio. All the oxygen-containing peaks, i.e. CO, CO_2 and H_2O were more narrow (not shown), which is the same effect as described in Section 3.2 by increasing the amount of oxygen in the feed. This is related to a faster production because of the extra oxygen available or to changed adsorption and desorption characteristics.

Fig. 10 shows the product responses obtained after pretreating the 0.3 wt% Rh/α-Al_2O_3 in pure O_2 instead of in a CH_4/O_2 mixture. This means that no steady state is obtained. The product spectrum shown is obtained after several methane/oxygen pulses because the first pulses gave very small conversions

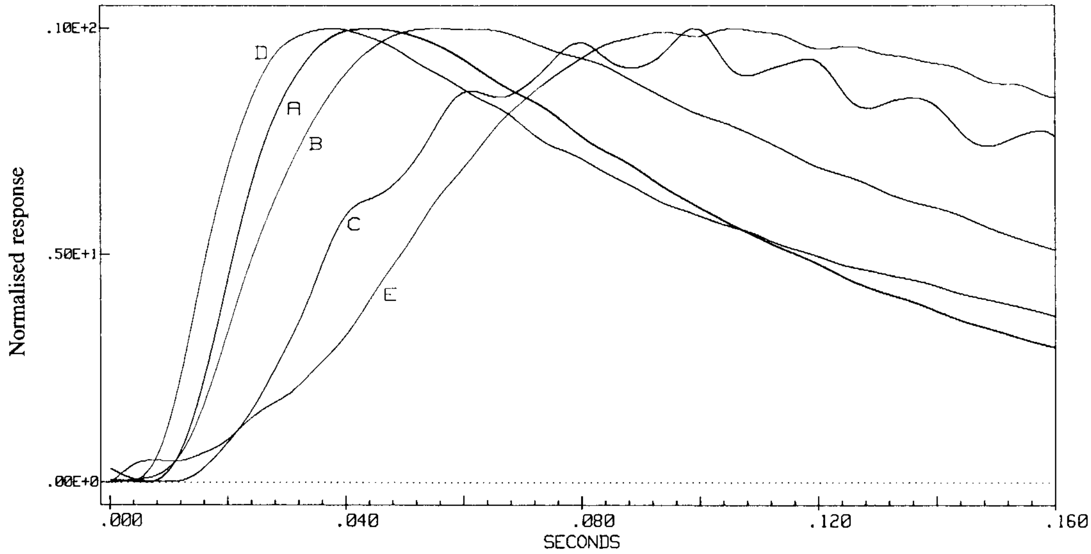

Fig. 9. Normalized responses on CH_4 pulsing over a Rh sponge diluted with α-Al_2O_3 (1 : 10) at steady state after CH_4/O_2=2 pretreatment. A, Ar; B, CO; C, CO_2; D, H_2; and E, H_2O.

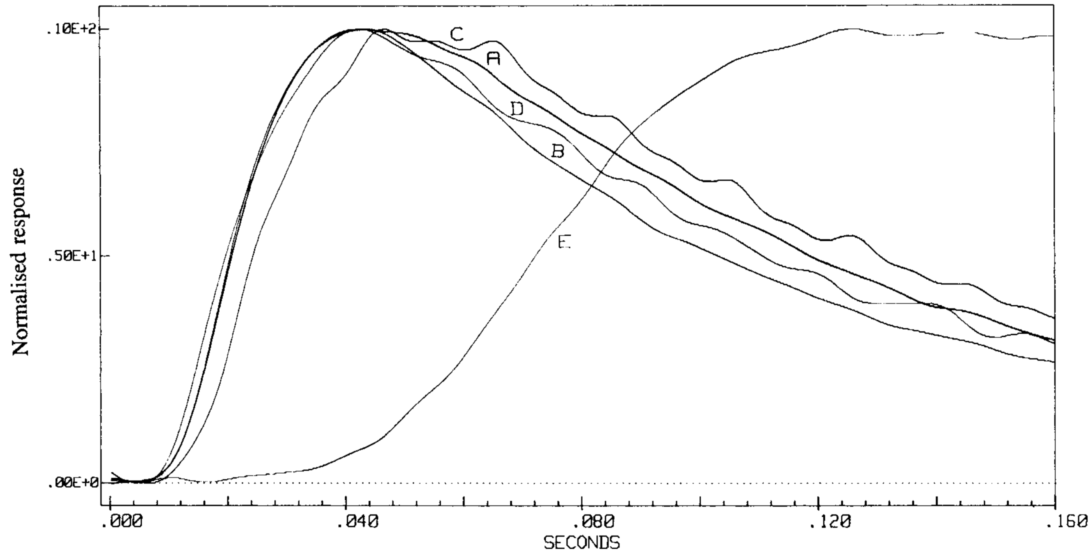

Fig. 10. Normalized responses on CH_4/O_2=2 pulsing over a 0.3 wt% Rh/α-Al_2O_3 after O_2 pretreatment. A, Ar; B, CO; C, CO_2; D, H_2 and E, H_2O.

as discussed earlier. The starting points of CO, CO_2 and H_2 are now very close, but CO_2 still has a small delay compared to CO. It is seen that all curves, except that of H_2O, which is quite similar to previous experiments, appear closer together. Again this is a consequence of more oxygen available for the CO and CO_2 formation. The more narrow H_2 response must be related to changing adsorption and desorption characteristics.

It should also be mentioned that some experiments showed CO and CO_2 responses having exactly the same starting point, rise time and decay curve. In the

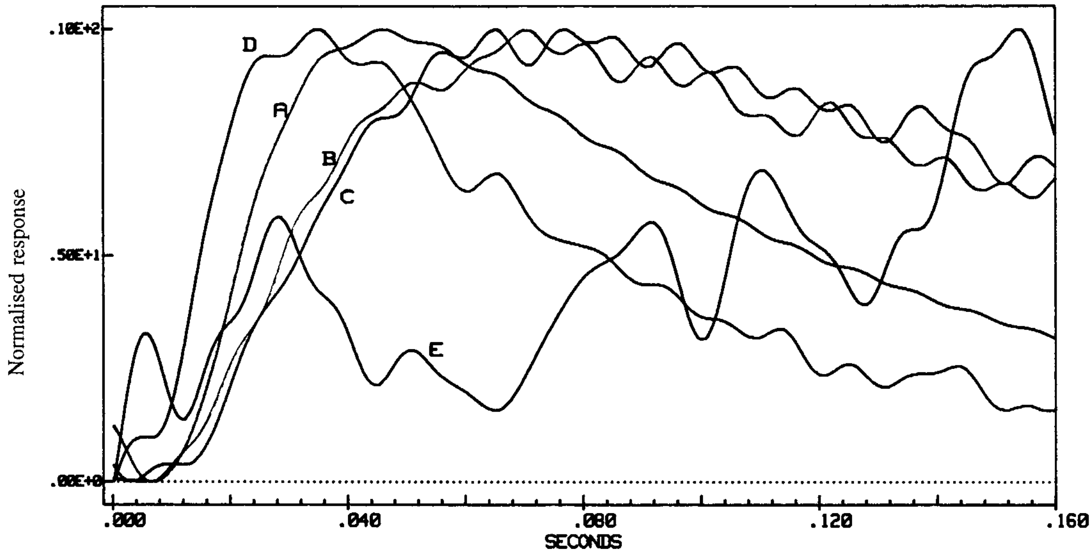

Fig. 11. Normalized responses on CH_4 pulsing over Rh sponge diluted with α-Al_2O_3 (1 : 10) pretreated in O_2 and a continuous flow of CH_4/O_2=1. A, Ar; B, CO; C, CO_2; D, H_2; and E, H_2O.

experiments where the Rh sponge diluted with α-Al_2O_3 was exposed to a continuous flow of CH_4/O_2 of a ratio of 1 : 1 (Section 3.2) the CO and CO_2 responses were similar (not shown). In this case, as discussed in Section 3.2, no sudden rise could be observed in the methane conversion until small amounts of pure methane were pulsed. By following the responses upon the first initial small CH_4 pulse, CO and CO_2 curves fell in parallel as shown in Fig. 11. The amount of available oxygen in this experiment was probably quite large because steady state was not obtained and the methane pulse was small.

It is concluded that the primary products are dependent on the amount of oxygen available. It is probably not directly dependent on whether a support is introduced or not. However, a support may provide an extra pool of oxygen and in this manner CO_2 and H_2O are more easily formed as primary products.

4. Conclusions

Blank experiments on an α-Al_2O_3 support showed no activity for the partial oxidation of methane in the 673–1123 K range. Oxygen multipulse experiments on the 0.3 wt% Rh/α-Al_2O_3 and on the pure support showed that α-Al_2O_3 is not inert concerning adsorption, desorption and storage of oxygen.

Totally oxidized catalysts show low activity because of few sites for methane dissociation and mainly the total oxidation products CO_2 and H_2O are formed. The formation of these products partially reduce the catalyst and with time-on-stream a steep discontinuity is found in the methane and oxygen conversion as reduced metal sites largely increase the rate of methane dissociation. The discontinuity is followed by a continuous change in the product distribution from CO_2 and H_2O towards CO and H_2. The time scale on which an active catalyst was obtained increased with increasing amount of oxygen in the feed. The time was also dependent on the catalyst system. Rh sponge mixed with SiC showed the shortest time, Rh sponge mixed with α-Al_2O_3 showed a longer time and Rh/α-Al_2O_3 showed the longest time-on-stream for obtaining an active catalyst. The latter indicates a spillover effect of oxygen from the support to the metal which also affects the methane conversion and syngas selectivity at steady state. The CO, CO_2 and H_2O pulse responses shifted to shorter times with increasing amount of oxygen in the feed, while H_2 showed the opposite effect. This indicates a faster formation of the products containing oxygen but sorption effects may not be excluded. Removal of surface oxygen by methane pulsing led to oxygen migration from the Rh bulk resupplying oxygen on the surface.

At conditions of pseudo steady state, CO and H_2 are formed as primary products on a Rh sponge mixed with SiC. Experiments on Rh sponge mixed with α-Al_2O_3 or a Rh/α-Al_2O_3 catalyst showed the same product sequence and unless sorption effects disguise the real primary product formation the sequence is not altered by the support. It is believed that the formation of primary products depends on the amount of oxygen available on the surface.

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