

An investigation on the reaction mechanism for the partial oxidation of methane to synthesis gas over platinum

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The partial oxidation of methane to synthesis gas has been investigated by admitting pulses of pure methane, pure oxygen and mixtures of methane and oxygen to platinum sponge at temperatures ranging from 973 to 1073 K. On reduced platinum the decomposition of methane results in the formation of surface carbon and hydrogen. No deposition of carbon occurs during the interaction of methane with a partly oxidised catalyst. Oxygen is present in three different forms under the conditions studied: platinum oxide, dissolved oxygen and chemisorbed oxygen species. Carbon monoxide and hydrogen are produced directly from methane via oxygen present as platinum oxide. Activation of methane involving dissolved oxygen provides a parallel route to carbon dioxide and water. Both platinum oxide and chemisorbed oxygen species are involved in the oxidation of carbon monoxide and hydrogen. In the presence of both methane and dioxygen at a stoichiometric feed ratio the dominant pathways are the direct formation of CO and H₂ followed by their consecutive oxidation. A Mars–van Krevelen redox cycle is postulated for the partial oxidation of methane: the oxidation of methane is accompanied by the reduction of platinum oxide, which is reoxidised by incorporation of dioxygen into the catalyst.

Keywords: partial oxidation of methane; platinum; synthesis gas; transient kinetics; Mars–van Krevelen; redox

1. Introduction

Different mechanisms for the partial oxidation of methane to synthesis gas have been proposed in the literature. At a methane to oxygen molar ratio of 2, i.e. the stoichiometric feed ratio, and temperatures ranging from 793 to 1173 K thermodynamic equilibrium was achieved on 25 wt% Ni/Al₂O₃ [1], 10 wt% refractory

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supported Ni [2], mixed metal oxides of Ru [3] and various supported transition metals [4,5]. On these catalysts the reaction is generally considered to occur in two stages [1–3]. First, CH_4 is oxidised to CO_2 and H_2O . At the stoichiometric feed ratio for synthesis gas production O_2 is the limiting reactant and is completely converted. Next, synthesis gas is produced via secondary reactions, either the steam and CO_2 reforming reactions [1,2] or the steam reforming and reverse water–gas shift reactions [3]. Baerns and coworkers postulated that CO_2 is formed as a primary product and that the formation of CO proceeds via a fast reaction of surface carbon species with CO_2 , i.e. the reversed Boudouard reaction, on 1 wt% Rh/ $\gamma\text{-Al}_2\text{O}_3$. Furthermore, OH groups in the support are also involved in the CH_x conversion to CO via a reforming reaction [6,7]. Choudhary et al. attribute selectivities to CO and H_2 higher than equilibrium values on NiO–CaO [8], 18.7 wt% Ni/ Al_2O_3 [9], Ni/ Yb_2O_3 [10], CoO/rare earth oxides [11] and Co/MgO [12] at temperatures lower than 973 K and a residence time of 10^{-2} s to primary formation of synthesis gas. However, Dissanayake et al. [13] attribute this observation to a hot spot in the catalyst bed, i.e. to a difference between the measured and the actual reaction temperature. Hickman and Schmidt [14–16] reported CO and H_2 as primary products applying adiabatically operated Pt- and Rh-coated monoliths at outlet temperatures of about 1300 K and residence times between 10^{-4} and 10^{-2} s. Simulations, based on a model of 19 elementary reaction steps, provided a theoretical basis for this observation [17]. Lapszewicz and Jiang [18] concluded that CO and CO_2 are produced in parallel over transition metal(s) supported on metal oxide(s) in the temperature range of 873 to 1173 K. A similar mechanism is suggested by Matsumura and Moffat [19] using a 10 wt% Ru/ SiO_2 catalyst.

The nature and reactivity of different oxygen forms on platinum have been investigated by various authors [20–43]. Adsorbed atomic oxygen predominates between 150 and 500 K [25,27–29]. The incorporation of oxygen occurs between 800 and 1200 K [21–26,30] and two different forms are reported. The first is dissolved or subsurface atomic oxygen [20,26,30,40–42] and the second concerns platinum oxide, either PtO [22] or PtO_2 [24,31,38]. The oxide can be several layers thick, with significant diffusion of oxygen atoms into the bulk [32,33,39]. Three different states of oxygen on platinum were also reported during the oxidation of CO between 300 and 700 K [41]. The reactivity of clean and oxidised Pt towards the adsorption of H_2 and CO is different [34,35]. The oxidised Pt creates higher binding energy states for both H_2 and CO, with a change in the initial sticking coefficient. Impurities, particularly Si, segregate to the surface and become oxidised at approximately 1000 K leading to the formation of an oxide phase, which seems non-reactive towards CO and H_2 [36,37].

The objective of the present study was to investigate the reaction mechanism of the partial oxidation of methane over platinum and the role of different oxygen species by means of a transient kinetic study.

2. Experimental set-up and procedures

2.1. TEMPORAL ANALYSIS OF PRODUCTS SET-UP

A temporal analysis of products (TAP) set-up was applied, which has been described in detail elsewhere [44]. The microreactor of the TAP set-up is a batch-wise operated fixed bed reactor with a typical residence time of 100 ms. Mass spectrometry is used to follow the outlet responses towards pulses of reactants admitted at the inlet with a submillisecond time resolution. It allows the study of catalytic sequences in detail, even at a high conversion. A limited amount of molecules is admitted to the catalyst surface leading to information on the interaction of the reactants with the surface at a well defined state of the latter. The shape of a response towards a pulse is determined by the various processes occurring in the microreactor: Knudsen diffusion, adsorption, desorption and reaction. Each response has a unique rise time, peak maximum and decay curve. A plot of the responses as a function of time contains in principle information on the reaction network. A secondary product has a response with a larger rise time than a primary product and the peak maximum is observed later. Adsorption and desorption processes result in a shift of the peak maximum towards a larger time value. Its position is also determined by the molecular weight of the component via the Knudsen diffusion coefficient.

The continuous flow mode of operation of the microreactor was applied for pre-treatment of the catalyst and determination of the absolute calibration factors. The latter allows to convert the mass spectrometer signal into mole per second.

Three different types of transient experiments were performed. The first is referred to as a *pulse experiment*, during which the response to a single pulse is measured at a fixed atomic mass unit (AMU) value.

The second type is an *alternating pulse experiment*, also called pump-probe experiment [44]. Two single pulses are introduced and the response is monitored at a fixed AMU value. The time interval between the two single pulses may be varied by the user and leads in principle to information on the life time of adsorbed species, which are created during the first single pulse and probed with a suitable reactant during the second single pulse.

In both the pulse and the alternating pulse experiment pulses are repeated and the responses are averaged to improve the signal to noise ratio. The repetition time is sufficiently large to avoid accumulation of adsorbed species at the surface.

The third type concerns a *multipulse experiment*. A series of single pulses is introduced and the responses of all pulses are monitored separately, i.e. without signal averaging, at a fixed AMU value. The time interval between two single pulses is variable and must be larger than the average residence time in the reactor. During a multipulse experiment the interaction of a component with the surface is followed at different degrees of surface coverage.

2.2. MATERIALS AND CATALYST CHARACTERISATION

The gases used were methane (99.9995%), oxygen (99.995%), hydrogen (99.999%), argon (99.99995%) and carbon monoxide (99.997%) from Air Products. The catalyst applied was platinum sponge (Johnson Matthey) with a grain size of 0.25–0.35 mm. The BET surface area of the fresh catalyst amounted to $0.050 \text{ m}^2 \text{ g}^{-1}$. Non porous $\alpha\text{-Al}_2\text{O}_3$ was used as inert packing material with a grain size of 0.25–0.30 mm.

The catalyst has two important advantages for the present study. Firstly, no support is used to avoid interactions between platinum and a support material. Secondly, internal pore diffusion limitations can be neglected, which ensures a more reliable data evaluation.

The amount of surface platinum atoms and of platinum oxide was determined in situ. The former followed a multipulse experiment of oxygen at a temperature of 373 K over a surface covered with carbon monoxide. The response of CO_2 was monitored and the corresponding surface area provided the amount of CO_2 molecules formed which is considered identical to the number of surface platinum atoms. The specific surface area, based on a theoretical amount of 1.3×10^{19} platinum atoms per square meter, was shown to be identical to that determined ex situ by the BET method. The amount of platinum oxide was determined by a multipulse reduction by hydrogen. The response of water was measured from which the amount of incorporated oxygen was deduced.

The catalyst was pretreated in situ during 2 h at a temperature of 1123 K with a continuous flow of oxygen followed by a flow of hydrogen. After the pretreatment the specific surface area had decreased to $0.035 \text{ m}^2 \text{ g}^{-1}$ and remained constant during the various experiments to follow. Prior to each experiment the catalyst was treated at reaction temperature with a continuous flow of oxygen, unless mentioned otherwise, after which it was kept under a pressure of 10^{-5} Pa during 10 min.

2.3. EXPERIMENTAL PROCEDURE AND DEFINITIONS

The inconel microreactor, with a length of 42 mm and an inner diameter of 6 mm, was charged with 0.20 g of catalyst and packed with inert material at each end. Two thermocouples were inserted inside the catalyst bed for temperature measurements. The axial temperature difference inside the bed was always lower than 5 K.

In all experiments argon was added to the admitted gases as a reference component for calculation of the amount of admitted molecules and of the conversion of the reactants. The number of methane molecules admitted per pulse amounted to 5×10^{15} , resulting in an average total pressure of 100 Pa above the catalyst surface during 100 ms. Gas phase reactions can be neglected at these conditions. The ratio of admitted methane molecules in a single pulse to the theoretical number of surface

platinum atoms was 0.05. During a multipulse experiment of oxygen 1×10^{16} molecules were admitted per pulse.

Temperatures ranging from 973 to 1073 K were investigated. The detected reaction products were H_2 , H_2O , CO and CO_2 . No formation of C_2 products was observed. For each experiment the conversion (X) and selectivities (S) as well as the carbon, hydrogen and oxygen balance (ϵ) were calculated, according to the following equations:

$$X_{CH_4} = \frac{n_{in,CH_4} - n_{out,CH_4}}{n_{in,CH_4}},$$

$$S_{H_2} = \frac{n_{out,H_2}}{n_{out,H_2} + n_{out,H_2O}},$$

$$S_{CO} = \frac{n_{out,CO}}{n_{out,CO} + n_{out,CO_2}},$$

$$\epsilon_C = \frac{n_{out,CH_4} + n_{out,CO} + n_{out,CO_2} - n_{in,CH_4}}{n_{in,CH_4}},$$

$$\epsilon_O = \frac{2n_{out,O_2} + n_{out,CO} + 2n_{out,CO_2} + n_{out,H_2O} - 2n_{in,O_2}}{2n_{in,O_2}},$$

$$\epsilon_H = \frac{4n_{out,CH_4} + 2n_{out,H_2} + 2n_{out,H_2O} - 4n_{in,CH_4}}{4n_{in,CH_4}},$$

where n is the total amount of moles (mol). The carbon and hydrogen balance mostly showed an accuracy better than 7%. Errors up to 15% are considered to be acceptable due to the accuracy of the absolute calibration factor. The conversion of methane was always nearly complete, unless specified otherwise.

3. Results and discussion

3.1. INTERACTION OF OXYGEN WITH THE CATALYST

Following the review by Engel and Ertl [20], the three different forms of oxygen, which are reported in various publications [20–33,38–43], are referred to as platinum oxide, dissolved oxygen and chemisorbed oxygen species.

The interaction of oxygen with the catalyst was investigated by multipulse experiments. In this case, the catalyst was completely reduced prior to the experiment. Initially oxygen was not detected quantitatively. This can be attributed to the formation of platinum oxide. At a temperature of 1023 K the amount formed was 6 wt% or equivalent to 900 theoretical monolayers of atomic oxygen. The platinum oxide was stable during a period of at least several hours, as indicated by the

immediate breakthrough of oxygen in a subsequent multipulse experiment. However, platinum oxide in the form of PtO or PtO₂ could not be detected by an ex situ XRD analysis.

The responses of a subsequent multipulse experiment are shown in fig. 1. The surface area of the oxygen responses initially increases and finally remains constant. The initial increase is due to oxygen interacting strongly with the catalyst, which is assigned to the presence of dissolved oxygen. The total amount of dissolved oxygen, as derived from the oxygen balance during the multipulse experiments, is equivalent to 0.7 theoretical monolayers of atomic oxygen at a temperature of 973 K and increases to 2.5 theoretical monolayers at a temperature of 1073 K. After a time interval of five minutes at 10⁻⁵ Pa this second type of oxygen species is completely removed. Five minutes is too long for the amount of dissolved oxygen involved to cause a signal above the noise level.

The peak maximum of each individual response of oxygen shifts to a larger time value than the peak maximum of the argon response, see fig. 2, which points to a third type of oxygen species interacting with the catalyst. This species, assigned as dissociatively chemisorbed oxygen, desorbs completely within two seconds, as expected from a typical activation energy for desorption of 217 kJ mol⁻¹ [17].

3.2. INTERACTION OF METHANE WITH THE REDUCED CATALYST

The interaction of methane with the catalyst was investigated by introducing a single pulse of methane. In this case the catalyst was completely reduced prior to the experiment. The residence time of methane amounted to 0.2 s and that of hydrogen to 0.4 s. No formation of carbon monoxide, carbon dioxide, ethane and ethene was observed. The carbon balance was significantly negative, while the

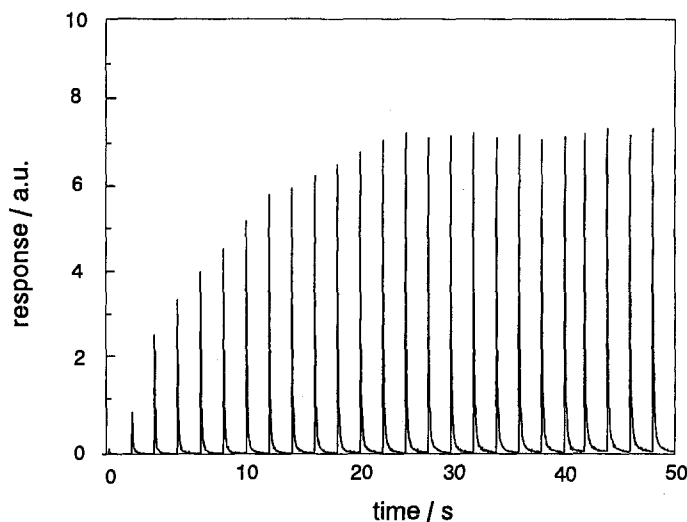


Fig. 1. Response of oxygen as a function of time. Multipulse experiment of oxygen at 973 K.

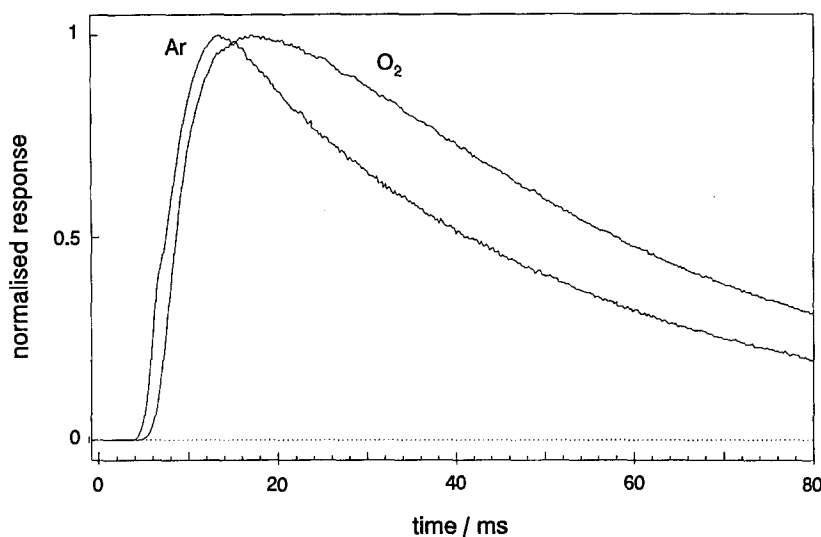


Fig. 2. Normalised responses of argon ($\times 4.5$) and oxygen as a function of time. Pulse experiment of argon and oxygen at 1023 K.

hydrogen balance was closed within 5% or less, indicating that formation of surface carbon occurred. The conversion of methane increased from 47% at a temperature of 944 K to 82% at 1023 K. The overall activation energy for the methane decomposition amounted to 52 kJ mol^{-1} , which is in good agreement with values reported for transition metal surfaces [45–50].

3.3. INTERACTION OF METHANE WITH PLATINUM OXIDE AND DISSOLVED OXYGEN

The interaction of methane with platinum oxide and dissolved oxygen was investigated with pulse experiments of methane alone. Pulsing of methane was started at a time interval of either 10 s or 10 min after the treatment with oxygen. In the latter case only oxygen in the form of platinum oxide is available, whereas in the former also dissolved oxygen species are present.

The normalised responses of CH_4 , CO , CO_2 , H_2 and H_2O when pulsing methane 10 min after the treatment with O_2 are shown in fig. 3. H_2 is observed earlier than H_2O and CO earlier than CO_2 . These results show that CO is the primary carbon containing and H_2 is the primary hydrogen containing product on platinum oxide. This was confirmed by a multipulse experiment of methane under similar conditions. Totally 5×10^{19} molecules were introduced into the reactor. The conversion of methane decreased from 95 to 64%, while the selectivities to CO and H_2 increased from 45% and 39% to 100%.

Applying the time interval of 10 s after the treatment with oxygen the reaction pathways depend on the dissolved oxygen concentration. The latter was varied by

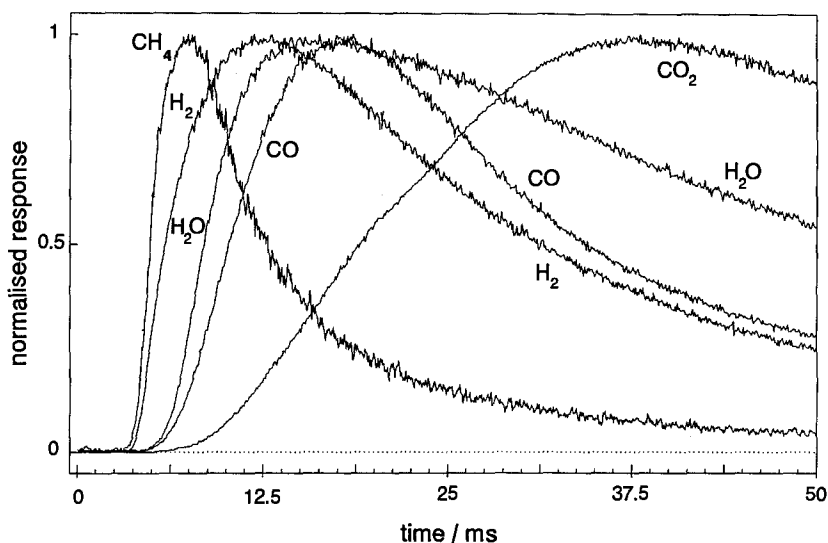


Fig. 3. Normalised responses of CH_4 ($\times 46$), CO ($\times 1.3$), CO_2 ($\times 1.2$), H_2 and H_2O ($\times 1.5$) as a function of time. Methane pulse experiment at 1023 K, 10 min after the oxygen treatment.

admitting an adapted amount of methane prior to the experiment. Fig. 4 shows the normalised responses of CH_4 , CO , CO_2 , H_2 and H_2O when prior to the experiment 5% of the dissolved oxygen was removed. The response of CO_2 has two maxima. The first maximum is observed before that of CO , which means that CO_2 is a

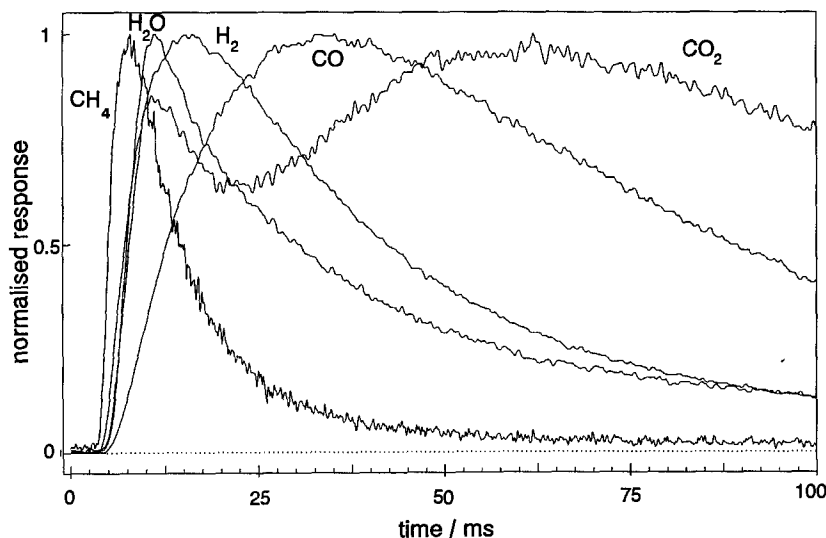


Fig. 4. Normalised responses of CH_4 ($\times 59$), CO ($\times 2.1$), CO_2 ($\times 8.3$), H_2 and H_2O ($\times 3.1$) as a function of time. Methane pulse experiment at 1023 K, 10 s after the oxygen treatment. Prior to the experiment 5% of the dissolved oxygen was removed.

primary product. The direct formation of CO_2 involves dissolved oxygen species. The formation of CO is attributed to the interaction of methane with oxygen present as platinum oxide. CO_2 is also a secondary product from CO as should be concluded from the second maximum in the CO_2 response. Both H_2O and H_2 are primary products, since H_2O is observed earlier than H_2 .

It is concluded that parallel reaction paths exist for the formation of CO and CO_2 as well as for H_2 and H_2O by involvement of different forms of oxygen.

3.4. INTERACTION OF METHANE WITH CHEMISORBED OXYGEN SPECIES AND VICE VERSA

The role of chemisorbed oxygen species was investigated with alternating pulse experiments of oxygen and methane and vice versa. An admitted methane to oxygen molar ratio of 0.5 was used to ensure complete reoxidation of the catalyst. Nine different time intervals were applied. The oxygen balances were reasonable in all cases.

Firstly, an experiment starting with oxygen was carried out. Chemisorbed oxygen species created during the first pulse are completely desorbed after a time interval of 2 s. Varying the time interval between the two pulses from zero up to 2 s resulted in an increase in the selectivity to CO from 1 to 7%. The corresponding selectivity to H_2 increased from 4 to 18%. These results show that chemisorbed oxygen species are involved in non-selective reaction paths. At a time interval of 9 s the selectivities to CO and H_2 amounted to 17 and 26% due to the disappearance of dissolved oxygen.

Secondly, an experiment starting with methane was performed, the time interval being varied between zero and 0.5 s. The selectivity to CO increased from 2 to 16% and the corresponding value for H_2 from 4 to 24%. Fig. 5 shows the normalised responses of CH_4 , CO, CO_2 , H_2 and H_2O at a time interval of 0.03 s. The responses of CO_2 and H_2O show two maxima. Carbon dioxide is a primary product, since the first maximum in the CO_2 response is observed before the response of CO. As soon as oxygen is introduced the formation of CO_2 increases, resulting in a second maximum, while the formation of CO abruptly decreases. A similar behaviour appears from the responses of H_2O and H_2 . These observations indicate that chemisorbed oxygen species catalyse the consecutive oxidation of CO and H_2 .

In the case of a time interval of 0.5 s the oxygen was introduced when gaseous methane was not present anymore in the catalyst bed. No formation of carbon containing reaction products was observed during the interaction of oxygen with the surface, which means that long living reactive carbon species are not present at the surface.

3.5. SIMULTANEOUS INTERACTION OF METHANE AND OXYGEN WITH THE CATALYST

The simultaneous interaction of methane and oxygen with the catalyst was inves-

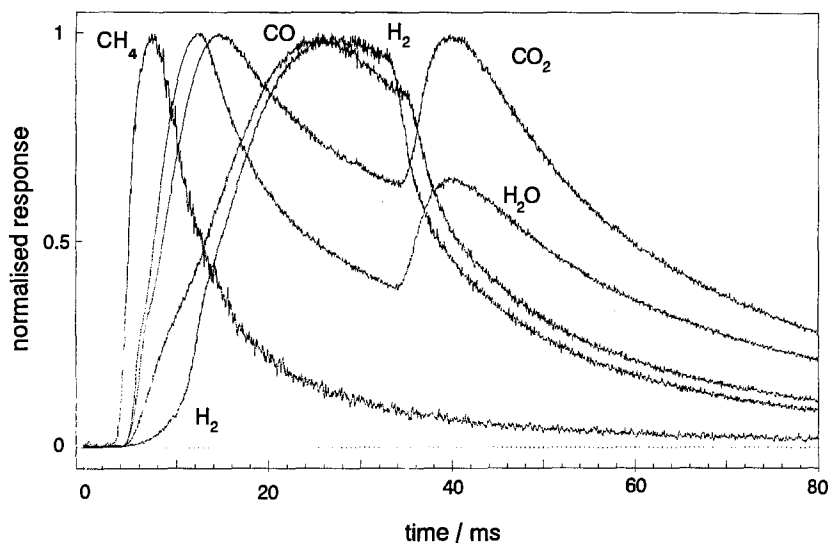


Fig. 5. Normalised responses of CH_4 ($\times 33$), CO ($\times 2.6$), CO_2 (1.2), H_2 ($\times 1.8$) and H_2O as a function of time. Alternating pulse experiment starting with methane followed by oxygen at a time interval of 0.03 s. Admitted methane to oxygen molar ratio of 0.5 and a temperature of 1023 K.

tigated by pulse experiments at a stoichiometric feed ratio. Oxygen was not detected quantitatively. The selectivities to CO and H_2 as well as the oxygen balances are shown in table 1. The excess in the oxygen balances indicates that oxygen present as platinum oxide is incorporated into the reaction products. The selectivities to hydrogen and carbon monoxide decrease at increasing reaction temperature.

A reasonable oxygen balance was obtained by admitting an adapted amount of methane prior to the experiment at a temperature of 1023 K. The selectivity to CO and H_2 increased to 69 and 88%. The normalised responses of CH_4 , CO, CO_2 , H_2 and H_2O are shown in fig. 6. The shape of the normalised responses of CO and H_2 is nearly identical. The response of H_2 is observed before H_2O , which means that H_2 is a primary product. CO_2 is observed later than CO, indicating that CO is a primary product.

A pulse experiment with a stoichiometric feed ratio performed over a reduced catalyst showed no significant formation of CO and CO_2 . The oxygen is incorpo-

Table 1

Selectivities to CO and H_2 and oxygen balances when methane and oxygen are pulsed simultaneously at a stoichiometric feed ratio

T (K)	S_{CO} (%)	S_{H_2} (%)	ϵ_{O} (%)
973	46	62	102
1023	42	51	160
1073	31	30	185

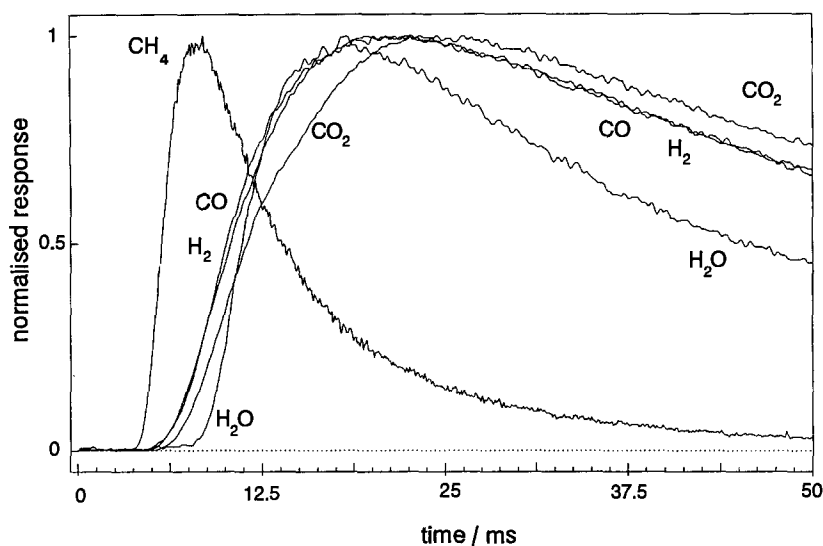


Fig. 6. Normalised responses of CH_4 ($\times 6.4$), CO ($\times 1.1$), CO_2 (2.4), H_2 and H_2O ($\times 5.3$) as a function of time. Simultaneous pulse experiment of methane and oxygen at 1023 K and a stoichiometric feed ratio. The catalyst was partly reduced by methane prior to the experiment.

rated into the catalyst, which indicates that platinum oxide has to be present for the formation of synthesis gas.

The incorporation of oxygen present as platinum oxide in the reaction products was verified by simultaneous pulsing of CH_4 and $^{18}\text{O}_2$ at a stoichiometric feed ratio. During the first pulses C^{16}O , $\text{C}^{16}\text{O}^{18}\text{O}$, C^{16}O_2 , H_2^{16}O and H_2^{18}O were produced, but C^{18}O and C^{18}O_2 were not detected quantitatively. CO is only produced via ^{16}O oxygen present in the form of platinum oxide. Chemisorbed oxygen species are only incorporated into CO_2 in the form of $\text{C}^{16}\text{O}^{18}\text{O}$, which confirms their role in the consecutive oxidation of CO . The percentage of $^{18}\text{O}_2$ oxygen incorporated into the reaction products only amounts to 3%, the major oxidation products being C^{16}O_2 and H_2^{16}O . The reaction mainly proceeds via oxygen present as platinum oxide, while the gaseous oxygen reoxidises the catalyst.

Finally, the carbon balances indicate that no deposition of carbon occurred during the interaction of methane with a partly oxidised catalyst. XPS and EDS studies on a used catalyst could not reveal the presence of carbon.

3.6. REACTION MECHANISM

The reaction network of the partial oxidation of methane to synthesis gas over platinum is illustrated in fig. 7.

Methane dissociates on reduced platinum to surface carbon and hydrogen atoms. No deposition of carbon occurs during the interaction of methane or

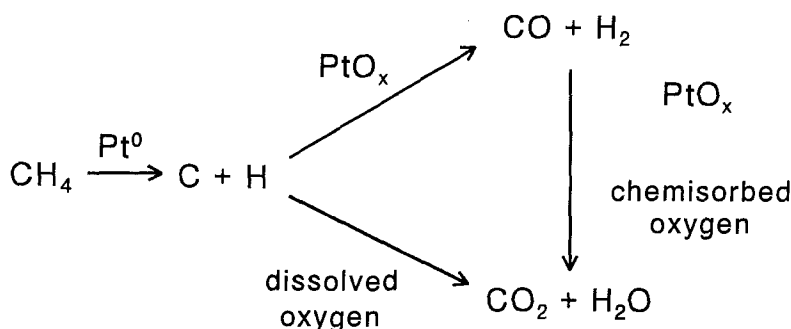


Fig. 7. Reaction network for the partial oxidation of methane to synthesis gas in the presence of oxygen over platinum sponge at temperatures between 973 K and 1073 K. Partially reduced PtO_x is reoxidised by dioxygen.

methane/oxygen with a partly oxidised catalyst. Reactive carbon species with a long lifetime are not present either at the surface.

The existence of a solid mixed phase containing PtO_2 as well as Pt was reported by Peuckert and Bonzel [38], who studied the decomposition of platinum oxide under ultrahigh vacuum conditions. This phase seems stable up to a temperature of 1100 K. Niehus and Comsa [23] reported that the first layer of oxidised platinum consists of platinum atoms. The Auger spectrum of the oxide remained unchanged even after heating to 1300 K.

The direct formation of CO from methane occurs via oxygen present as platinum oxide, which also favours the recombination of two H atoms to produce H_2 . In parallel to this reaction, methane is directly converted to CO_2 and H_2O by involvement of dissolved oxygen. This involvement requires segregation of the dissolved oxygen species to the surface, where it reacts with methane. In this case the dissolved oxygen acts as a reservoir for chemisorbed oxygen, but a type with a reactivity different from that of the species already referred to as chemisorbed oxygen. Rigas et al. [51] suggest that dissolved oxygen species modify the electronic properties of the surface and thus change the reactivity of adsorbed oxygen species for the ethylene epoxidation on silver powder. A mechanism for oxygen segregation is proposed by Lauterbach et al. [40], who studied the reaction between subsurface oxygen and CO as well as H_2 on Pt(100). The reaction is assumed to occur at the border between the subsurface oxygen region and the surrounding region where CO or H_2 is adsorbed. In this region the subsurface platinum phase is restructured and this process uncovers subsurface oxygen atoms, which in turn react with the chemisorbed CO or H_2 .

The consecutive oxidation of CO and H_2 occurs via oxygen present as platinum oxide and via chemisorbed oxygen species. For platinum oxide the consecutive reaction is more pronounced at increasing temperature.

In the presence of both methane and oxygen at a stoichiometric feed ratio the dominant reaction pathways are the direct formation of CO and H_2 followed by the

consecutive oxidation to CO_2 and H_2O . The reaction proceeds via a redox cycle mechanism proposed by Mars and van Krevelen [52] for selective oxidation reactions. The oxidation of methane is accompanied by the reduction of platinum oxide, which is reoxidised by incorporation of dioxygen into the catalyst.

4. Conclusions

The partial oxidation of methane was investigated applying a temporal analysis of products set-up. The short residence time of the reactants in the catalyst bed allowed us to investigate the interaction of methane and oxygen with the surface at an initial stage of the reaction. Unique information on the lifetime and reactivity of adsorbed species could be obtained. Three different oxygen forms, corresponding to dissociatively chemisorbed oxygen, dissolved oxygen and platinum oxide, are present during the interaction of oxygen with platinum sponge. The decomposition of methane on reduced platinum results in the formation of surface carbon and hydrogen. Carbon monoxide and carbon dioxide are produced in parallel from methane by involvement of different oxygen species.

In the presence of both methane and oxygen at a stoichiometric feed ratio the dominant reaction pathways are the direct formation of CO and H_2 followed by their consecutive oxidation. A Mars–van Krevelen redox cycle is postulated for the partial oxidation of methane over platinum.

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