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Rhodium-catalyzed partial oxidation of methane to CO and H_2. Transient studies on its mechanism

O.V. Buyevskaya [b], D. Wolf [a] and M. Baerns [a,1]

[a] *Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*
[b] *Boreskov Institute of Catalysis, Novosibirsk 630090, Russia*

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The reaction of methane with surface oxygen as well as the interaction of methane/oxygen mixtures with a Rh(1 wt%)/γ-Al_2O_3 catalyst was studied by applying the temporal-analysis-of-product (TAP) reactor. The product distribution was strongly affected by the degree of surface reduction. CO_2 is formed as a primary product via a redox mechanism with the participation of surface oxygen. The dehydrogenation of methane yielding carbon deposits on the surface occurs on reduced surface sites. The formation of CO proceeds with high selectivity (up to 96%) at 1013 K via fast reaction of surface carbon species with CO_2.

Keywords: partial oxidation of methane; synthesis gas; Rh/γ-Al_2O_3; transient-study; temporal analysis of products

1. Introduction

Direct partial oxidation of methane to synthesis gas is a promising alternative to conventional steam reforming due to its mild exothermicity and lower $H_2 : CO$ ratios in the gas obtained. It was first shown by Prettre et al. [1] that synthesis gas can be produced from methane and oxygen using a supported nickel catalyst in the temperature range from 735 to 900°C with yields close to those predicted by thermodynamics. Similar results were obtained more recently over catalysts containing noble metals [2,3]. Only limited attention has been given to the reaction mechanism. However, the factors determining the formation of the primary products are a subject of great interest. The overall mechanism of this process is often considered to involve two stages: (1) catalytic combustion of methane to CO_2 and H_2O in the oxygen-rich zone of the reactor and (2) reforming of the remaining CH_4 by H_2O and/or CO_2 produced in the first stage [1–4]. Recently, Schmidt and co-workers [5,6] have shown that synthesis gas can be produced with high yields (80–85%) by oxidation of methane over monolith-supported metals in an autothermal flow reac-

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[1] To whom correspondence should be addressed.

tor at 1000°C and residence times of ca. 10 ms. Simulations carried out by these authors [6] for Rh- and Pt-coated alumina monoliths on the basis of a 19-elementary-steps model led to the assumption that under CH_4-rich conditions and high temperatures, H_2 and CO are the primary products of methane oxidation. In contrast, Matsumura and Moffat [7] have shown that at short contact times deep oxidation occurs but also significant formation of CO and H_2 which can be explained by secondary reactions of CH_4 reforming which proceed effectively due to the high surface temperature of the catalyst.

In the present work, an attempt is made to elucidate the heterogeneous reaction steps of methane oxidation over an alumina supported Rh catalyst in terms of formation of primary products applying a transient pulse technique in the temporal-analysis-of-products (TAP) reactor. The methane/surface interaction was investigated in the absence and in the presence of oxygen in a wide range of surface coverages by active oxygen species and carbon deposits. Furthermore, the reaction of CO_2 and O_2 with surface carbon species formed by methane decomposition was examined in order to elucidate the reaction pathway to CO. Although the temperature applied was lower than in the previous studies it is believed that this might be partly considered an advantage; the results may reveal reaction steps which might not be detectable any more at high temperature because of their high rate.

2. Experimental

2.1. CATALYST

Rh(1 wt%)/γ-Al_2O_3 (S_{BET} = 91.4 $m^2\ g^{-1}$) was prepared by incipient wetness impregnation of γ-Al_2O_3 (Degussa) previously calcined at 873 K for 14 h using an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey) as precursor. After impregnation the catalyst was dried at 373 K for 2 h and exposed to a flow of hydrogen at 773 K for 2 h; 100 mg of the catalyst (d_p = 250–355 μm) were charged to the reactor. The metal surface area of 1.1 $m^2\ g^{-1}$ and the metal dispersion of 43% were determined by CO adsorption at room temperature. For data evaluation an adsorption stoichiometry (CO/Rh ≈ 1.3) was estimated from DRIFTS.

2.2. REACTOR SYSTEM

The pulse experiments were carried out in the temporal-analysis-of-products (TAP) reactor described elsewhere in detail [8,9]. Pulses containing a small amount of reactant (10^{15}–10^{17} molecules/pulse) were injected via two high-speed valves into the reactor, which contained the catalyst (approximately 10^{18} Rh sites) between two layers of quartz. The response to the inlet signal at the reactor outlet was monitored as concentration of the detected compound versus time with a resolution down to 10 μs.

Prior to the experiments, the catalyst was oxidized by pulsing oxygen at 1013 K until a stable response was observed. Thereafter, it remained exposed to vacuum conditions (10^{-4} Pa) for 20 min in order to remove adsorbed oxygen. The reaction of methane with surface oxygen was then studied at 1013 K by pulsing a CH_4/Ne(Kr) (9 : 1) mixture over the catalyst; pulse sizes between 0.8×10^{16} and 2.9×10^{16} molecules were applied. The influence of gas-phase oxygen on the reaction of methane was studied by simultaneous pulsing of CH_4/Ne(Kr) (9 : 1) and O_2/Ne = (9 : 1) mixtures from two valves. The reactions of CO_2 and oxygen with carbon deposits were investigated at 1013 K by pulsing CO_2 or O_2 over the catalyst surface which was previously pretreated by pulsing of methane. Simultaneous and sequential pulsing of CH_4/Kr (9 : 1) and CO_2/Ne (1 : 1) mixtures with time intervals between 0.5 and 120 s were applied to elucidate the reactivity of carbon species of different lifetimes.

For mass spectroscopic identification of the different compounds the following atomic mass units (AMU) were used: 84 (Kr); 44 (CO_2); 32 (O_2); 30 (C_2H_6); 28 (CO_2, CO, C_2H_6, C_2H_4); 26 and 25 (C_2H_6, C_2H_4); 20 (Ne); 16 and 15 (CH_4); 14 (CH_4, CH_2); 2 (H_2). The fragmentation patterns and relative sensitivities of all components were experimentally determined and used for data evaluation.

The gases employed were CH_4 (99.995%), O_2 (99.996%), CO_2 (99.995%), Kr (99.997%), Ne (99.99%) and H_2 (99.999%) from Messer-Griesheim (Oberhausen, Germany).

3. Results

3.1. CATALYTIC REACTION OF METHANE WITH OXYGEN

The dependences of methane conversion and product selectivities on the amount of methane molecules pulsed over the catalysts at 1013 K are given in figs. 1a and 1b. CO_2 was the only observable product in the reaction of methane with the oxidized Rh catalyst (see fig. 1a). It can be assumed that water formed was not detected in the TAP experiments due to its slow desorption or to the formation of surface hydroxyl groups. Pulsing of methane resulted in the consumption of active oxygen, i.e., in an increase of the degree of surface reduction. This, in turn, led to a change in the product composition: after pulsing of 6×10^{18} CH_4 molecules over ca. 10^{18} Rh sites, CO was the main product and no significant amount of carbon deposits was formed, as can be derived from the carbon balance. It should be noted that the pure γ-Al_2O_3 showed no activity towards methane conversion. The amount of oxygen reacting with methane up to the state of maximum CO selectivity is higher than that corresponding to the completely oxidized surface rhodium (Rh^{3+}). In the following the term "surface oxygen" characterizes the active oxygen sites, including, however, lattice oxygen from the rhodium bulk, and low coordinated oxygen from the carrier as well.

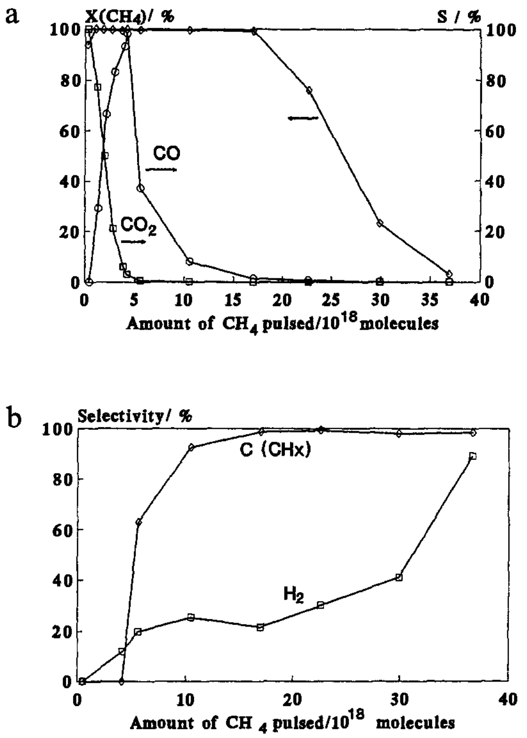

Fig. 1. (a) Dependence of CH_4 conversion X and selectivities S of CO and CO_2 on the amount of methane molecules pulsed over Rh(1 wt%)/Al_2O_3 at 1013 K. (b) Dependence of carbon deposit and hydrogen selectivities on the amount of methane molecules pulsed over Rh(1 wt%)/Al_2O_3 at 1013 K.

Further pulsing of methane resulted in a decrease in CO yield and in significant carbon formation on the surface (see fig. 1b).

Additional information concerning the reaction pathways can be derived from the analysis of the response shapes. The response of CO_2 on reacting of methane with the initial surface was rather narrow (cf. fig. 2, curve A). It was shown above that reaction of methane with the initial catalyst led only to CO_2 formation while reaction of methane on the partly reduced surface, i.e., in the presence of reduced sites, resulted in CO and surface carbon species. The responses of CO and CO_2 during the reaction of methane over the partly reduced surface are shown in fig. 2 (curves B and C). It can be seen that both curves have the same shape, i.e., these two products appeared at the reactor outlet simultaneously. Further reduction of the catalyst surface by methane resulted in the slower formation of CO being the only carbon-containing product after pulsing more than 5×10^{18} CH_4 molecules as illustrated by its broader response (see fig. 3). Reaction of methane after pulsing of $>1 \times 10^{19}$ CH_4 molecules yielded mainly the formation of carbon species (cf. fig. 1b) until the coverage by carbon deposits was so high that almost no methane was consumed. CH_2 species were detected in the gas phase (AMU= 14)

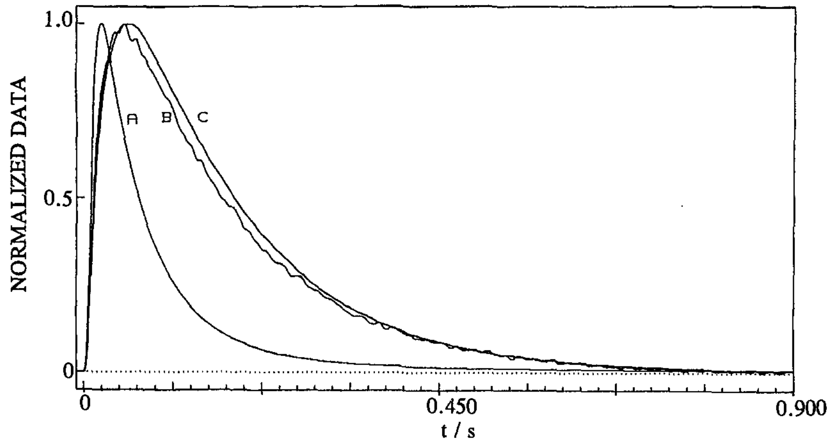

Fig. 2. Normalized responses of CO_2 and CO at the reactor outlet when pulsing CH_4 over Rh(1 wt%)/Al_2O_3 at 1013 K: (A) CO_2 in the reaction of methane with initial catalyst; (B) CO in the reaction of methane after pulsing of 4×10^{18} CH_4 molecules; (C) CO_2 in the reaction of methane after pulsing of 4×10^{18} CH_4 molecules.

after pulsing 1×10^{19} CH_4 molecules. This was derived when accounting for the fragmentation pattern of methane.

Different types of H_2 responses depending on the degree of the reduction were observed in the present work. No hydrogen was detected in the reaction of methane with the initial catalyst surface. Over the partly reduced surface, hydrogen was formed but its response was broad (cf. fig. 4, curve A) indicating a slow process of formation or desorption. Further reduction of the surface resulted in a significant change in the shape of hydrogen response. The narrow peak with a maximum at 25–35 ms (cf. fig. 4, curve B) showed fast formation and desorption of hydrogen

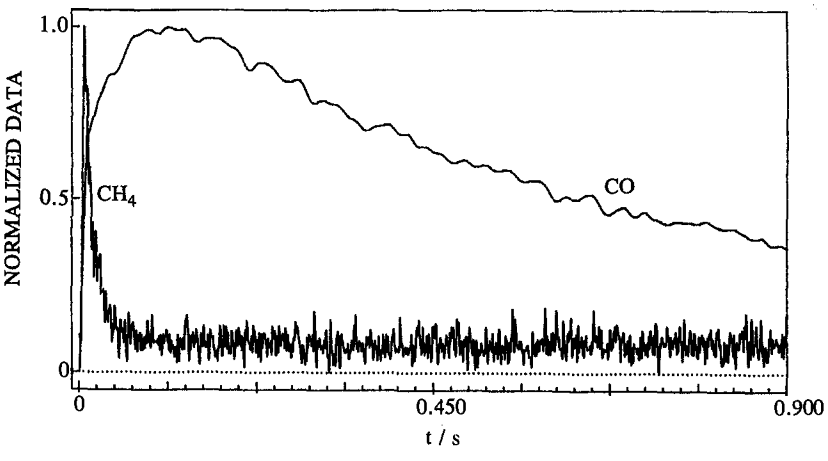

Fig. 3. Normalized responses of CH_4 and CO in the reaction of methane with Rh(1 wt%)/Al_2O_3 after pulsing of 1×10^{19} CH_4 molecules at 1013 K.

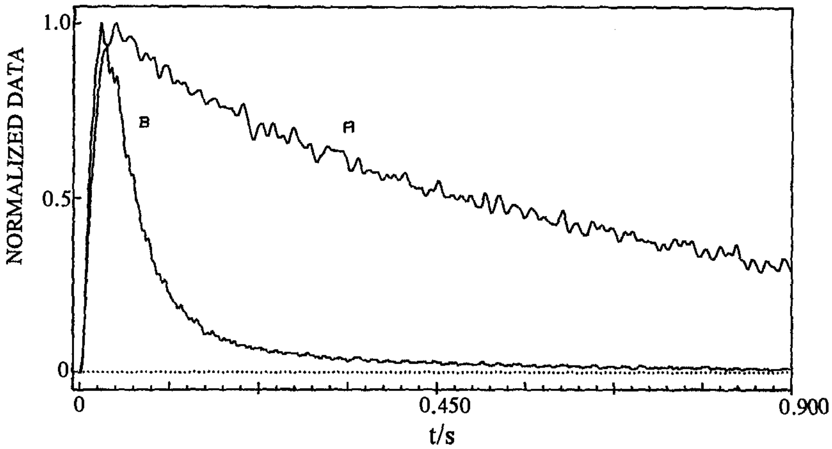

Fig. 4. Normalized responses of H_2 during reaction of methane over catalyst surfaces after pulsing of different amounts of CH_4 molecules. (A) 5×10^{18} CH_4 molecules; (B) 3.7×10^{19} CH_4 molecules.

over the highly reduced surface; this reflects the initial reaction step of C–H bond dissociation in the methane molecule.

In order to elucidate the reason of the different shapes of H_2 response, hydrogen was pulsed over the catalyst surfaces pretreated by different amounts of methane. Hydrogen oxidation occurred significantly over the partly reduced surface and was accompanied by a broad response of unconverted H_2. However, during pulsing of hydrogen over the highly reduced surface covered by carbon deposits, its response became more narrow and similar to the response of hydrogen formed by methane decomposition over reduced surface (cf. fig. 4, curve B).

Additional experiments were also performed to study the possibility of hydrogen formation by secondary reactions, e.g., by the reaction of water with surface carbon deposits. No formation of hydrogen was observed in these experiments.

3.2. REACTION OF METHANE/OXYGEN MIXTURES

The influence of the gas-phase oxygen on the reaction of methane was studied using simultaneous pulsing of methane and oxygen over the catalyst with different degrees of surface reduction, i.e., pretreated by pulsing different amounts of CH_4 molecules. It should be noted that product formation in the presence of gas-phase oxygen did not differ from that in the reaction of methane with surface oxygen. Fast formation of CO with a yield of 73% was observed in the reaction of a CH_4/O_2 (2.6 : 1) mixture over the partly reduced catalyst, i.e. pretreated by pulsing of 5×10^{18} CH_4 molecules. The shapes of the CO and CO_2 responses were similar in this case and relatively narrow as it was observed for the reaction of methane with surface oxygen (see fig. 2, curves B and C). Hydrogen was not detected in these experiments. The reaction of a methane/oxygen mixture (2.6 : 1) over a catalyst surface previously reduced by pulsing of 3.7×10^{19} CH_4 molecules resulted in the formation of hydrogen with a yield of 32% while the only carbon-containing product, i.e. CO, was formed with $Y = 11.6\%$ ($X_{CH_4} = 99.7\%$). The remaining methane was converted to carbon deposits as derived from the carbon balance. Respective responses for this reaction are given in fig. 5. It can be seen that methane decomposition resulting in the formation of hydrogen is very fast, as can be derived from the narrow hydrogen response ($t_{max} = 0.15$ s). This response has the same shape as the H_2 curve in the reaction of pure methane over the highly reduced surface, which proceeds most probably via dissociation of CH_4. The desorption of CO under this condition occurred during more than 2 s.

3.3. REACTION OF O_2 AND CO_2 WITH SURFACE CARBON SPECIES

The reaction of oxygen with surface carbon species obtained by the decomposition of methane was investigated by pulsing of O_2. Complete conversion of oxygen was always observed while only 2.6–5% of oxygen introduced was detected in the products (CO_2 and CO) at the reactor outlet, the remainder of oxygen was consumed for catalyst reoxidation. These results showed that reaction of oxygen with surface carbon species formed by methane decomposition cannot be considered the main reaction pathway in CO formation.

No CO_2 dissociation on the catalyst surface without carbon deposits was observed. The results of simultaneous and separate pulsing of CH_4 and CO_2 showed no influence of CO_2 on methane conversion, i.e., the initial step of CH_4 decomposition is not affected by the presence of CO_2. The reaction of CO_2 to CO was observed only in the presence of carbon deposits. For this reaction, CO produced by pulsing of CO_2 had the same mean surface residence time as unconverted CO_2 (see fig. 6). The reactivity of carbon species of different lifetimes was studied by the sequential pulsing of CH_4 and CO_2 with different time intervals between pulses. Results

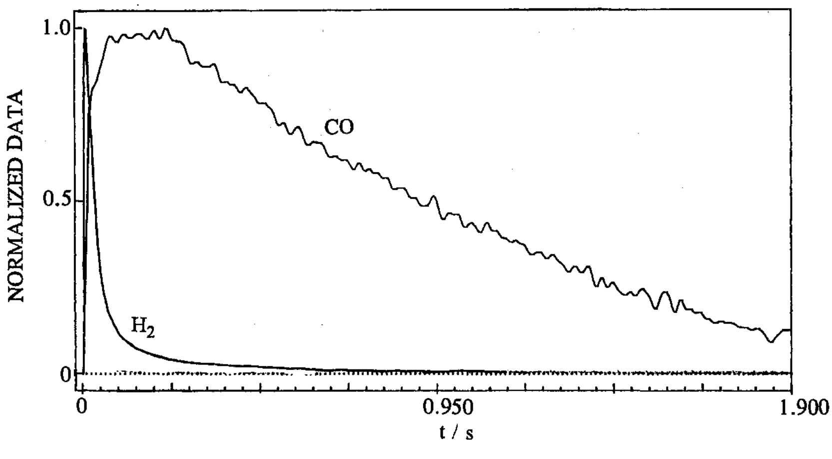

Fig. 5. Normalized responses of H_2 and CO in the reaction of methane/oxygen mixture ($CH_4/O_2 = 2.6$) over catalyst surface pretreated by pulsing of 3.7×10^{19} CH_4 molecules.

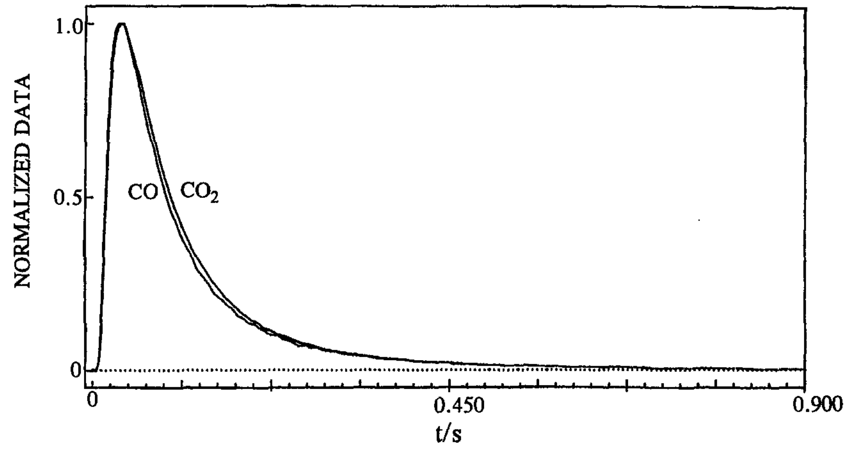

Fig. 6. Normalized responses of CO_2 and CO during reaction of CO_2 with surface carbon deposits on the Rh(1 wt%)/Al_2O_3 at 1013 K.

of these experiments are given in table 1 and illustrate the high reactivity of the carbon deposits, especially immediately after methane decomposition.

4. Discussion

High conversion of methane (X_{CH_4} >99%) was observed in the absence of any gas-phase oxygen. From the results on methane reaction with the Rh/Al_2O_3 surface presented in figs. 1a and 1b it follows that the degree of reduction of the catalytic surface strongly affects the reaction pathways in the reaction of methane with the catalyst surface. The response of CO_2 to the pulse of methane reacting with the oxidized surface was rather narrow indicating the fast formation of CO_2 most probably as a primary product (cf. fig. 2, curve A). When comparing these results with those of the reaction of methane/oxygen mixtures, it can be concluded that the overall reaction occurs via a redox mechanism and the role of gas-phase oxygen is to replenish the active sites on the surface after depletion of oxygen due to reaction with methane. The nature of active oxygen (oxygen bonded to metal sites or to the support) is not yet quite clear. Oxygen species besides those bonded to surface

Table 1
Conversion of CO_2 in the experiments with sequential pulsing of CH_4 and CO_2

Time interval between CH_4 and CO_2 pulses (s)	X_{CO_2} (%)
0.5	94
1.0	91
20.0	56
120.0	39

metal sites are involved in the reaction with methane. The amount of oxygen reacting with methane is even higher than that possibly originating from the completely oxidized bulk rhodium. Therefore, the involvement of oxygen sites of the carrier must be assumed. In situ DRIFTS studies [11] carried out in parallel with the present work indicated the consumption of surface OH groups on the Rh/Al_2O_3 catalyst during the influence of methane, which might be related to a reforming reaction on the surface:

$$CH_x + 2OH^- \rightarrow CO + [(x+2)/2]H_2 + O^{2-} \quad (x \leqslant 4)\,. \tag{1}$$

With respect to the nature of the primary reaction products, the following results of the response analyses should be taken into account. Based on the response sequence (see figs. 2 and 3) it can be assumed that CO is formed simultaneously with CO_2 because its response has the same shape as that of CO_2. Also in the reaction of methane with the partly reduced surface the formation of CO occurred as the only carbon-containing product. Thus, it might be tentatively assumed that CO is formed as primary product. However, for identifying the primary reaction steps in the methane partial oxidation, the interaction of CO_2 with the catalyst surface depending on the coverage by oxygen and carbon should be also considered. The fast reaction of CO_2 to CO was observed only in the presence of carbon deposits. CO produced by pulsing of CO_2 had the same mean surface residence time as unconverted CO_2 (cf. fig. 6). Thus, the formation of CO in the experiments with pulsing of methane can be also explained by surface reaction between carbon deposits and CO_2 which are most probably the primary products. Decomposition of methane to carbon species and hydrogen occurs on reduced surface sites while reaction of methane with surface oxygen results in CO_2 formation only. A scheme of the reaction mechanism derived from the transient experiments described above is presented in fig. 7.

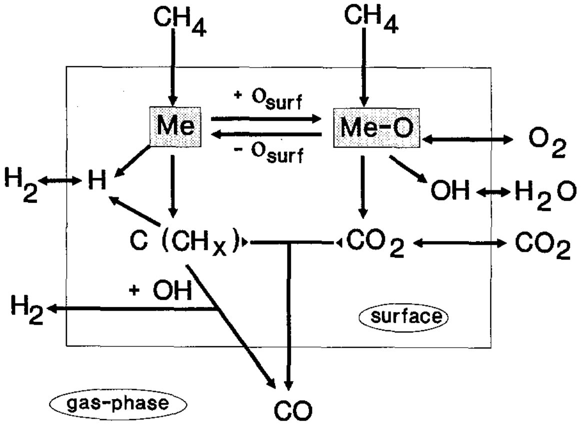

Fig. 7. Scheme of the initial surface reaction steps in the partial oxidation of methane to syngas.

The nature of carbon species formed on the surface by methane decomposition (C or CH_x) is still an open question. The model of Hickman and Schmidt [5] lumps the breaking of all four C–H bonds into one step of direct carbon formation as a reaction intermediate. However, the participation of carbon deposits containing hydrogen (CH_x) in reactions leading to CO and H_2 cannot be excluded. The reaction of CH_x species was proposed by Oh et al. [10] for methane oxidation over alumina-supported noble metal catalysts at lower reaction temperatures:

$$CH_{x(x=2\,\mathrm{or}\,3)} + O \rightarrow HCHO \rightarrow CO + 2H, \quad 2H \rightarrow H_2 . \tag{2}$$

This proposition is supported by results obtained in the present study. CH_2 species (see fig. 8) were detected in the gas phase. Despite the fact that only trace amounts of CH_2 were detected, this result may be considered as an indication that CH_x species are involved in the reaction pathway. As shown by sequential pulsing of CH_4 and CO_2, the reactivity of carbon deposits depends on their lifetime. It can be assumed that active carbon species (containing hydrogen) initially formed by interaction of methane with the catalyst surface are transformed into less active ones probably by sequential dehydrogenation.

The primary formation of hydrogen by decomposition of methane was derived from the present results. The broad response of hydrogen observed in the reaction of methane over the partly oxidized surface can be explained by its slow desorption based on the comparison with results on the interaction of pure hydrogen with the catalyst surface. The dissociation of methane on the reduced metal sites seems to be the main reaction pathway for hydrogen formation under the transient conditions applied since no hydrogen was observed in the reaction of gas-phase H_2O with carbon deposits. However, as was indicated by the in situ DRIFTS studies [11] mentioned above surface OH groups are consumed probably by a reforming reaction leading to CO as well as H_2.

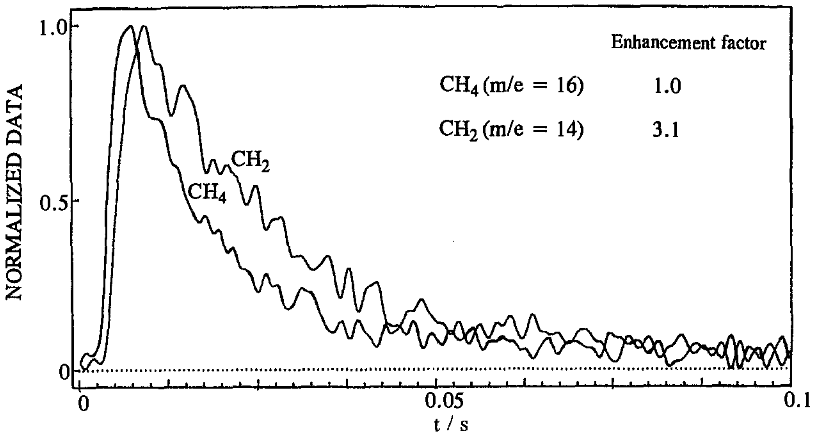

Fig. 8. Normalized responses of CH_4 and CH_2 during reaction of methane over catalyst surface pretreated by pulsing of 10^{19} CH_4 molecules.

5. Conclusions

Reaction pathways in the partial oxidation of methane to CO and H_2 are strongly affected by the degree of surface reduction. Oxidation of methane occurs via a redox mechanism with participation of lattice oxygen. The formation of CO proceeds with high yield via a fast reaction of surface carbon species with CO_2 (reverse Boudouard reaction), which are the primary products of the reaction of methane with reduced and oxidized surface sites, respectively. Hydrogen can be formed as primary product by dehydrogenation of CH_4 on the reduced surface sites; however, its secondary formation cannot be excluded especially under steady-state conditions. The following reactions are important for high CO production and stable catalyst performance:

$$CH_4 \rightarrow CH_x + (4-x)H \rightarrow C_s + 4H, \quad 4H \rightarrow 2H_2 \tag{3}$$

$$CH_4 + 4[O]_{surface} \rightarrow CO_2 + 2H_2O \tag{4}$$

$$CO_2 + C_s \rightleftharpoons 2CO \tag{5}$$

$$CH_x + 2[OH]_{surface} \rightarrow CO + [(x+2)/2]H_2 + [O]_{surface} \, . \tag{6}$$

Referring to the steady-state condition, a tuned catalyst activity for methane dehydrogenation and its total oxidation is required. Considering the high sensitivity of the product distribution to the surface state, a very narrow range is expected for the optimum degree of surface reduction. A high degree of surface reduction is necessary for the formation of hydrogen with high yield as primary product.

The results discussed refer to a temperature of 1013 K. At higher temperatures the importance of the various reaction steps may certainly change; nevertheless, the scheme as such should stay valid.

In the present paper the derivation of the reaction mechanism was only illustrated for a Rh/γ-Al_2O_3 catalyst. It should be mentioned, however, that analogous results were obtained for Pd/γ-Al_2O_3, Ru/γ-Al_2O_3, and Pt/MgO, although there are differences in the activity for the particular reaction steps of total oxidation and dehydrogenation of methane.

Acknowledgement

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