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Primary reaction steps and active surface sites in the rhodium-catalyzed partial oxidation of methane to CO and H_2

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The nature of surface sites responsible for methane activation and CO_x formation on Rh catalysts for the partial oxidation of methane to syngas was investigated. The interaction of CH_4 with Rh-black after oxidative and reductive pretreatments was studied applying (a) pulse experiments at reduced total pressure (10^{-4} Pa) and 1013 K in the temporal-analysis-of-product (TAP) reactor and (b) in situ DRIFTS at 973 K. The saturation of the metal surface sites with oxygen was found to inhibit methane dissociation. Direct methane oxidation to CO_2 on the oxidized surface sites proposed earlier was excluded. Methane is first dissociated on reduced surface sites; the carbon species formed, then, react with surface oxygen to CO_2. Rh sites responsible for methane activation are neither related to the formation of the Rh_2O_3 nor Rh^0. Probably the partially oxidized species (Rh^+) or highly dispersed Rh^{3+} entities act as active surface centers for the dissociation of methane. For supported catalyst, such sites are stabilized by the support, which on the other side acts as a source of active oxygen involved in the oxidation of surface carbon and hydrogen.

Keywords: partial oxidation of methane; synthesis gas; rhodium; oxygen species; transient study; DRIFTS

1. Introduction

Recent mechanistic studies of the partial oxidation of methane to synthesis gas over $Rh/\gamma\text{-}Al_2O_3$ have shown that the final product distribution (CO, H_2, CO_2, H_2O) is strongly determined by the degree of surface coverage by oxygen [1,2]. The secondary formation of CO via a reaction between surface carbon from methane dissociation and CO_2 was confirmed for the whole range of the degree of reduction while the formation of hydrogen as a primary product was found to occur on the highly reduced surfaces. From these studies, however, the active and optimal oxidation state of rhodium remained unclarified; in particular, further elucidation of the role of the support in the formation of active Rh sites was required. Furthermore, the questions arose whether a common pathway of methane activation for the formation of all products exists and whether the simultaneous existence of different oxidation states of Rh is required to promote both, initial and consecutive reaction steps.

To analyze the catalytic behaviour of Rh sites in the absence of the support, rhodium-black was investigated applying transient experiments in the temporal-analysis-of-products (TAP) reactor and in situ DRIFT spectroscopy. The experimental results on the interaction of CH_4 and CH_4/O_2 mixtures with Rh-black after oxidative and reductive pretreatments and related sequences of product formation were compared with corresponding results obtained for $\gamma\text{-}Al_2O_3$-supported Rh in the preceding studies [1,2].

2. Experimental

2.1. Catalysts

Rhodium-black (99.9%; Johnson Matthey) was used "as received" and after different pretreatments (see table 1). BET surface areas (S_{BET}), metal surface areas (S_{Me}) determined by CO adsorption at room temperature and phase compositions derived from XRD are summarized for the differently pretreated samples in table 1.

2.2. Transient studies

The pulse experiments were carried out in the temporal-analysis-of-products (TAP) reactor described elsewhere in detail [3,4]. Pulses of reactants (10^{14}–10^{18} molecules/pulse) were injected via two high-speed valves into the reactor ($L = 42$ mm, $D_{in} = 5$ mm), which contained 20 mg of Rh-black between two layers of quartz. All experiments were carried out at 1013 K. Pulse sizes between 2×10^{15} and 2.9×10^{16} molecules were applied; the responses of four to ten pulses were averaged. All gas mixtures contained 10% of an inert gas (Ne or Kr) as an internal standard.

The interaction of methane with Rh-black (as received) was studied after different pretreatments.

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Table 1
Results on characterization of Rh-black

Catalyst pretreatment	Phase composition from XRD	S_{BET} ($m^2 g^{-1}$)	S_{Me} ($m^2 g^{-1}$)
"as received"	metallic Rh	9.5	0.4
oxidized at 1023 K in 100 kPa O_2	Rh + Rh_2O_3(major)	15	0.04
reduced at 1000 K in 100 kPa H_2	metallic Rh	3.2	0.2

First, methane was pulsed over the catalyst which had been exposed to vacuum at 1013 K for 30 min. In a number of experiments, prior to pulsing methane, the catalyst was oxidized using continuous flow of O_2 at 1013 K. Thereafter, it remained exposed to vacuum (10^{-4} Pa) for 20 min. The interaction of methane with reduced surfaces was studied after pulsing hydrogen. Simultaneous pulsing of O_2 and CH_4 from two valves was applied in order to elucidate the role of gas-phase oxygen in the methane/surface interaction. The reactivity of surface carbon towards CO_2 was studied by sequential pulsing of methane and CO_2 with a time interval of 0.2 s. 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); 18 (H_2O); 15 (CH_4); 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%), CO (99.999%) and H_2 (99.999%) from Messer-Griesheim (Oberhausen, Germany).

2.3. Spectroscopic studies

For diffuse reflectance in situ IR measurements a Unicam RS FTIR spectrometer with a commercial diffuse reflectance accessory (Spectra Tech, Mod. 003-102) was used. The catalyst was first pretreated in a continuous stream N_2 at 973 K for 1 h. For the various experiments, the catalyst was further treated either by O_2 (20% in N_2) for 1 h at 973 K or by pure H_2 (3 ml/min) for 4 h at 973 K. After pretreatment with O_2 or H_2 the catalyst was purged continuously with N_2 for 30 min and the spectrum of the catalyst was recorded at 973 K. Then, the reaction mixture (5% CH_4 in N_2 or 5% CH_4 + 2.5% O_2 in N_2) was admitted at 973 K until constant band intensities were observed. The spectrum of the catalyst obtained before the introduction of the reaction gases was always subtracted from the spectra recorded during reaction, i.e. the final spectra represent only absorption bands of the adsorbed species and of the gases assuming that the spectrum was not changed by the presence of reactants. Spectra were recorded every minute (200 scans with a resolution of 4 cm^{-1}) starting with the admission of the reaction gases; this time interval depended on scan rate and resolution.

Gases of commercial purity N_2 (99.999%), CH_4 (99.995%) and H_2 (99.999%) were deoxygenated with an adsorptive oxygen trap. O_2 (99.995%) was used without further purification. The total flow rate was always 10 ml/min with the exception of the reduction in pure H_2 where catalyst was treated under static conditions.

3. Results and discussion

3.1. Methane activation and product distribution over Rh-black depending on the degree of reduction

Since pretreatment procedures of Rh-black, i.e. the selection of gaseous media (oxygen, hydrogen or vacuum), strongly determined the initial oxidation state of Rh, the solid-phase composition and the surface area (see table 1), the transient and spectroscopic studies on methane interaction with differently pretreated surfaces were performed to elucidate the nature of active sites involved in the methane dehydrogenation and in the formation of oxygen-containing products.

3.1.1. Rh-black "as received"

TAP results. Methane pulsed over Rh-black ("as received") after heating at 1013 K in vacuum (10^{-4} Pa) for 0.5 h reacted with surface oxygen being still present on the rhodium surface. This result is, however, not surprising against earlier work: For the oxygen interaction with single crystal Rh surfaces as well as with polycrystalline samples, in general, the following phenomena have been reported: (i) the initial adsorption rate of O_2 is high (sticking coefficients in the range between 0.62 and 1) at low temperatures (130–500 K) [5–8] and (ii) oxygen desorbs over a wide temperature range (700–1600 K) [5–7,9–11]. Thus, according to these results oxygen which has been adsorbed on Rh-black during its exposure to ambient atmosphere, might not have been completely desorbed under the conditions applied.

The dependences of CH_4 conversion and selectivities towards CO, CO_2, H_2 on the number of CH_4 molecules pulsed over Rh-black at 1013 K, which corresponded to an increasing degree of reduction, θ, are presented in fig. 1 (θ-value is estimated as a ratio of oxygen atoms consumed from the catalyst in the reaction with methane forming CO_x and H_2O to the total amount of oxygen atoms detected in the oxygen-containing products dur-

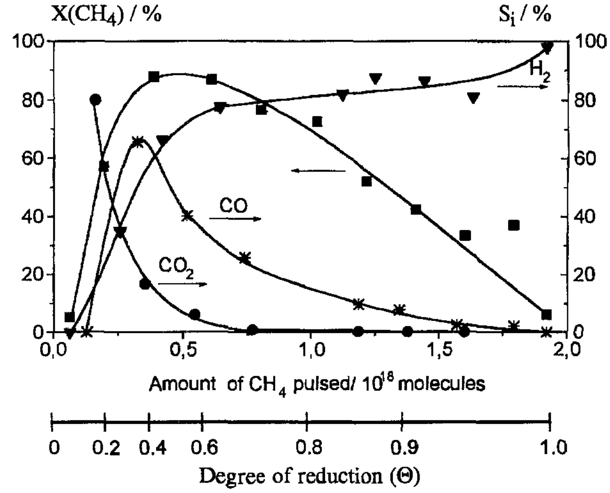

Fig. 1. Dependences of CH_4 conversion and product selectivities on the amount of CH_4 molecules pulsed at 1013 K over Rh-black ("as received") after heating at 1013 K in vacuum for 0.5 h.

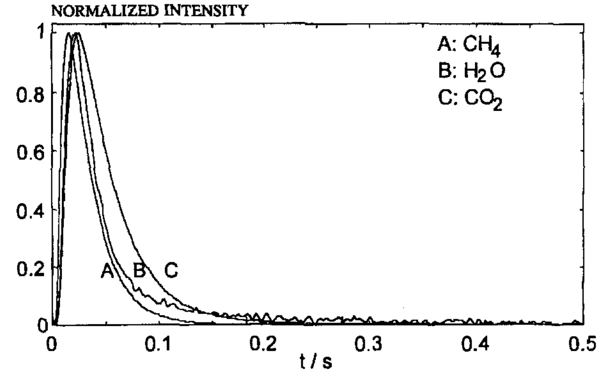

Fig. 2. Normalized responses of CH_4, CO_2 and H_2O in the reaction of methane with surface oxygen of Rh-black (cf. fig. 1) after pusing (1.6–2.6) × 10^{17} CH_4 molecules.

ing pulsing CH_4, which corresponded to approximately 1% of the total Rh atoms).

A distinct increase in CH_4 conversion from 5 to 88% was observed during pulsing 5 × 10^{17} CH_4 molecules ($\theta \leqslant 0.4$) but then a monotonous decrease was detected with the further pulsing ($\theta > 0.4$). Thus, methane conversion is inhibited by high coverage of the Rh surface by oxygen while low methane conversion at higher degree of reduction can be caused by different reasons, e.g. carbon deposition, decrease in metal surface area or changing the Rh oxidation state into an inert one.

Similar to Rh/γ-Al_2O_3 [1], the product distribution over Rh-black was significantly affected by the degree of reduction (cf. fig. 1). During pulsing of 2.5 × 10^{17} CH_4 molecules only CO_2 and H_2O were detected as products. It should be noted that, for γ-alumina-supported Rh, the only detectable product in the reaction of CH_4 with the oxidized catalyst was CO_2 whereas no direct monitoring of the H_2O formation was possible due to its slow desorption or formation of OH groups on the support surface [1]. For unsupported Rh, water formed by the oxidation of methane with surface oxygen desorbed fast as derived from the narrow H_2O response (see fig. 2); this allowed more exact estimation of the oxygen amounts consumed in the reaction with methane. With increasing degree of reduction selectivities to CO_2 and H_2O decreased coinciding with increased selectivity to CO and H_2. While CO selectivity passed through a maximum at approximately $\theta = 0.4$ a steady rise of H_2 selectivity with pulsing of methane was observed.

Methane interaction with Rh-black ($X_{CH_4} = 5\%$ during the first pulses) reveals a significant difference to the results on pulsing of methane over Rh/γ-Al_2O_3 where already 93% of CH_4 conversion initially occurred with a further increase up to 99.8%. The reaction scheme proposed in the previous work included the interaction of methane molecules with oxidized and reduced metal surface sites yielding CO_2 and surface carbon as primary products, respectively [1]. Present results on Rh-black, however, show that high coverage of the Rh surface by oxygen inhibits methane conversion. Thus, the direct formation of CO_2 via a reaction of methane with the oxidized surface center proposed in the previous study cannot be considered as a primary reaction step of methane interaction with Rh surfaces. Reduced metal sites are required for the methane activation, which most probably consists in methane dehydrogenation. When considering the results on methane interaction with the supported catalyst it can be proposed that reduced Rh sites are stabilized by support resulting in high methane conversion even after oxidative pretreatment. Further results on the activity of oxidized Rh sites in the oxidation of methane are presented below.

3.1.2. Rh-black after oxidation

Methane interaction with Rh-black after pretreatment in a continuous flow of O_2 was investigated using both, transient and spectroscopic techniques; the XRD pattern of the oxidized Rh-black showed the major presence of Rh_2O_3 along with metallic Rh (see table 1).

TAP results. Reaction of methane with Rh-black pretreated in O_2 at 1013 K resulted only in the formation of CO_2 and H_2O with a maximum yield of 3% during pulsing 8 × 10^{18} CH_4 molecules (table 2). By contrast, for the sample "as received", which contained only small amount of oxygen (approximately 1% of the total number of Rh atoms), the changes in the methane conversion and product distribution occurred during pulsing only 2 × 10^{18} CH_4 molecules (cf. table 2). For the oxidized catalyst, even more extended pulsing of methane did not result in an increase in the methane conversion and in the formation of syngas. These results show that the Rh_2O_3 phase present predominantly in the oxidized sample is inactive for the methane oxidation.

DRIFTS results. The interaction of CH_4 with oxidized Rh-black (fig. 3) at 973 K showed a rather high induction time of 5 min for the formation of gas-phase

Table 2
Surface titration with methane: X_{CH_4}, S_{CO}, S_{H_2} depending on the number of CH_4 molecules pulsed over Rh-black after different pretreatments

Pretreatment	Amount of pulsed CH_4 (10^{17} molecules)	X_{CH_4} (%)	S_{CO} (%)	S_{H_2} (%)
"as received", vacuum for 30 min at 1013 K	0.3–0.5	5	0	0
	4–6	88	40	68
	> 19	0	–	–
oxidation at 1013 K	< 80	3–5	0	0
partial reduction by H_2 pulsing at 1013 K of the oxidized sample ($O_{removed}/Rh_{total} = 0.22$)	0.3–1.2	93	25	16
complete reduction by H_2 pulsing at 1013 K	0.3–3.7	0	–	–

CO compared to supported Rh (1 min, ref. [2]) which is in agreement with a low activity for methane activation of the oxidized Rh surface observed in the TAP experiments. When a CH_4/N_2 stream was passed over the catalyst at 973 K after pretreatment with O_2 at 973 K only an absorption band at 2359 cm^{-1} due to CO_2 in the gas phase was observed after 1 min of exposure. The CO_2 band gained its maximum intensity only after 4 min of exposure time. After 5 min of methane exposure a CO band with two maxima at 2181 and 2085 cm^{-1} appeared indicating CO in the gas phase. After 10 min the CO_2 band was vanished. Simultaneously, absorption bands at 3014 and 1302 cm^{-1} due to CH_4 in the gas phase were observed. After 30 min the CO bands were also nearly vanished.

3.1.3. *Rh-black after reduction*

Since methane dehydrogenation was assumed to be the only initial reaction step in the partial oxidation of methane further information on the nature of active sites (metallic Rh or partly oxidized Rh species) responsible for the methane dissociation is desirable. Relating to this point the experiments on methane interaction with Rh-black after reductive pretreatments have been performed.

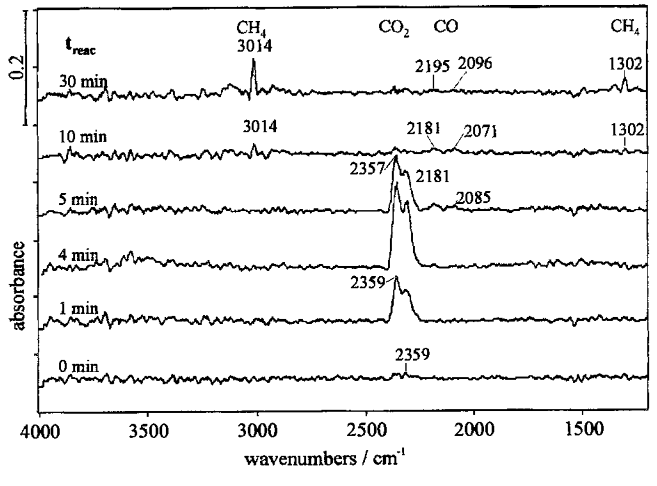

Fig. 3. DRIFTS spectra of adsorbates on the surface of Rh-black after O_2 pretreatment when exposed to CH_4 at 973 K after different reaction times (t_{reac}).

TAP results. Oxidized Rh-black, which showed low activity during pulsing 8×10^{18} CH_4 molecules (see above), was treated in situ at 1013 K by pulsing H_2; total conversion of H_2 to H_2O was observed on pulsing 2.3×10^{19} H_2 molecules; then the conversion of H_2 decreased but stayed rather high (55–60%). The amount of oxygen removed from Rh-black by this treatment corresponded to 2.6×10^{19} atoms or to an O-to-Rh ratio of approximately 0.22. The reaction of CH_4 after this partial reduction of Rh-black resulted in high CH_4 conversion of 93% (cf. table 2). Complete reduction was achieved by further H_2 pulsing until no conversion of H_2 was detected. This pretreatment caused a total deactivation of Rh-black towards methane dissociation, i.e., no conversion of methane occurred when methane was pulsed over the completely reduced sample.

DRIFTS results. When passing methane over the Rh-black after its heating in hydrogen at 973 K no formation of surface or gas-phase products was observed within 40 min time on stream. When a CH_4/O_2 mixture passed over the H_2-pretreated sample, the delay in the formation of CO_x products was observed compared to the reaction of CH_4 over the oxidized Rh-black. The CO_2 band intensity reached a maximum after 10 min of exposure. CO was observed after 20 min only. These results show that restoring of the activity of the reduced Rh-black during passing of a CH_4/O_2 mixture takes place due to the presence of oxygen in the reaction mixture. Taking into account a rather long induction period for the formation of products it should be assumed that the reduced form of Rh initially present after treatment with hydrogen was not active in the oxidation of methane.

One of the possible reasons of catalyst deactivation after reduction might be a loss in surface area. Considering, however, the metal- and BET-surface areas of two samples ("as received" and reduced) the decrease of S_{Me} from 0.4 to 0.2 $m^2\ g^{-1}$ and S_{BET} from 9.5 to 3.2 $m^2\ g^{-1}$ cannot explain the complete deactivation since the number of surface Rh sites decreased only by a factor of 2–3. Therefore, the reason of deactivation can be a destruction of active sites for methane conversion by complete catalyst reduction. Partially oxidized Rh, e.g. Rh^{1+}, or highly dispersed Rh^{3+} entities on the surface might be required for methane activation.

3.1.4. Summary on the role of Rh oxidation state in methane activation

Present results clearly demonstrated that oxidation of the Rh surface resulted in a loss of activity for the methane activation while the presence of oxygen in small amounts had a positive effect on catalyst activity toward the methane dehydrogenation. Since we observed the formation of CO_2 as the only carbon-containing product in the beginning of the reaction of methane with surface oxygen, the findings reported in the literature on the nature of active sites in the combustion of methane should be taken into account. A recent study of Burch and Loader [12] on methane oxidation on Pt/Al_2O_3 catalysts showed that the optimum rate of reaction corresponded to a platinum surface partially covered by both oxygen- and carbon-containing species and that dissociative adsorption of methane is accelerated by the presence of the remaining surface oxygen. As conclusion the authors postulated that neither a fully reduced nor a fully oxidized platinum surface is optimal for methane oxidation; instead, an intermediate degree of surface reduction is required. It should be noted that, however, platinum in the metallic state was proposed as the most active form in earlier studies [13,14]. Interesting results on the oxidation state of noble metal during high-temperature methane oxidation have been reported by Farrauto et al. [15]; they found that when only palladium metal is present no methane activity exists and that the presence of PdO is required. No similar investigations for Rh-containing catalysts are, however, known.

In our earlier transient study on Rh/Al_2O_3 catalyst, a small increase in the CH_4 conversion from 93% to > 99% with increasing number of CH_4 pulses was observed during the interaction of CH_4 with the oxidized surface [1]. This effect was less significant compared to unsupported Rh where only very low CH_4 conversion of 3–5% occurred during CH_4 pulsing over the oxidized surface (cf. table 2). This indicates that a much higher concentration of the surface sites responsible for CH_4 dissociation was available on the supported catalyst even after oxidation at 1013 K. Another difference in the reaction of methane over Rh-black and supported Rh is the amount of oxygen involved in the reaction with methane in the absence of gas-phase oxygen. When CH_4 was pulsed over Rh-black after its exposure to vacuum for 30 min, the amount of oxygen which reacted with CH_4 corresponded to an O-to-Rh ratio of 0.01. An attempt to increase the amount of reactive oxygen by oxidative treatment led to the formation of inactive surface. Contrary to Rh-black, a high amount of oxygen (O-to-Rh ratio > 1.3) was consumed from the supported catalyst in the reaction with CH_4 forming CO and CO_2. Thus, two effects of the support were derived:

- Metal sites responsible for CH_4 dissociation are stabilized by the support; oxidative treatment does not lead to deactivation due to Rh_2O_2 formation.
- High oxygen storage capacity of the support in addition to oxygen from rhodium for the reaction of carbon species to CO_2 is provided.

The nature of active metal sites involved in the dissociation of methane is, however, still an open question. On the basis of TAP and DRIFTS results on methane interaction with completely reduced Rh-black it can be assumed that fully reduced rhodium is most probably not involved in the dissociation of methane. The high catalyst activity of Rh-black always coincided with the presence of the small oxygen amounts when formation of partially oxidized Rh, e.g., Rh^{1+}, but no Rh_2O_3 phase formation can take place. In the case of the supported catalyst these centers can be stabilized by oxide support. More detailed studies on the Rh oxidation state in γ-alumina supported catalysts during the partial oxidation of methane to syngas applying in situ XPS and DRIFTS techniques are presently in progress.

3.2. The nature of the primary products

As mentioned above, the first step of CH_4 interaction with catalyst surface consists in its dissociation on the reduced surface sites. Contrary to our previous suggestion it is evident now that CO_2 is formed via the reaction of carbon deposits resulting from initial methane dissociation with surface oxygen and not via a direct interaction of methane with the surface oxygen. Although only CO_2 and H_2O were initially formed during the interaction of methane with the catalytic surface (cf. figs. 1 and 3), the elucidation of product sequence on the partly reduced surfaces when CO and H_2 are also produced requires the precise analysis of the product responses.

3.2.1. Sequence of CO, CO_2, H_2 and H_2O formation from methane

Contrary to Rh/Al_2O_3, where the formation of H_2O could not be directly monitored, all reaction products in the case of Rh-black were detected at the reactor outlet allowing the complete analysis of their response sequence. This analysis is based on the comparison of the surface residence times of products, which can be calculated from the measured first moments of the concentration responses at the reactor outlet. The first moment of the pulse response (t_P) reflecting the mean residence time in the TAP reactor is determined by diffusion time through the reactor and by residence time of the reactant on the surface due to adsorption, desorption and reaction processes. The gas transport in the range of pulse sizes applied occurred mainly by Knudsen diffusion:

$$\frac{\partial c}{\partial t} = -D_{\mathrm{K,eff}} \frac{\partial^2 c}{\partial x^2} \,. \qquad (1)$$

To evaluate the surface residence time the contribution of the diffusion time should be eliminated. According to diffusion theory diffusion time (t_D) through the reactor is determined by the molar mass M_p of the compound. Therefore, the diffusion times for various products can be calculated from the diffusion time of an inert gas (t_{inert}), which was present in the reaction mixture as an internal standard:

$$t_D = t_{inert}(M_p/M_{inert})^{1/2} . \qquad (2)$$

However, when comparing the diffusion times of the inert gas with that of reaction product it has to be taken into account that the diffusion of the inert gas starts at the reactor inlet and passes first the quartz layer while the product is formed within the catalyst bed. Since initially the concentration of the product is zero at both reactor inlet and outlet, its diffusion proceeds in both directions; this was accounted for in the reactor model [16]. In order to obtain an appropriate inert standard signal that can be compared to the measured product responses a simulation of the inert gas response has been performed assuming that the diffusion of inert gas starts at the center of the catalyst bed. The simulated inert gas response is illustrated in fig. 4; the diffusion coefficient was derived from the measured response (cf. fig. 4). The value of the first moment for the simulated inert gas response (t_{inert}^{sim}) was then used for the determination of the diffusion time of product (t_D) according to eq. (2).

The difference between total mean residence time in the reactor (t_P) and diffusion time for each product (t_D) reflects the delay due to surface processes, i.e., the surface mean residence time (t_S) can be estimated as:

$$t_S = t_P - t_D . \qquad (3)$$

The corresponding t_S values of the products CO_2, CO, H_2O and H_2 during the reaction of methane and methane/oxygen mixture with Rh-black are summarized in table 3. The surface residence times of the various products during pulsing methane were influenced by the degree of reduction. During the first pulses of methane when only CO_2 and H_2O were formed, the very short surface residence time of CO_2 (6 ms) showed its fast formation and desorption. From the experiments on pulsing CO_2 the surface residence time due to adsorption/desorption amounted to 3 ms indicating that no strong adsorption of CO_2 occurred. With increasing degree of surface reduction an increase in t_S-values for both CO and CO_2 was observed. After pulsing (3.8–5.7) × 10^{17} CH_4 molecules the t_S-values of CO and CO_2 amounted to 113 and 83 ms, respectively. The reduction of the surface, however, did not affect the adsorption–desorption processes during the interaction of CO and CO_2 with Rh-black as was derived from the separate pulsing of CO and CO_2. Taking this into account the observed high t_S-values for CO and CO_2 (cf. table 3) produced from methane should be determined mainly by their slower formation on the partly reduced surface. The higher value for CO compared to CO_2 must be, thus, ascribed to its secondary formation.

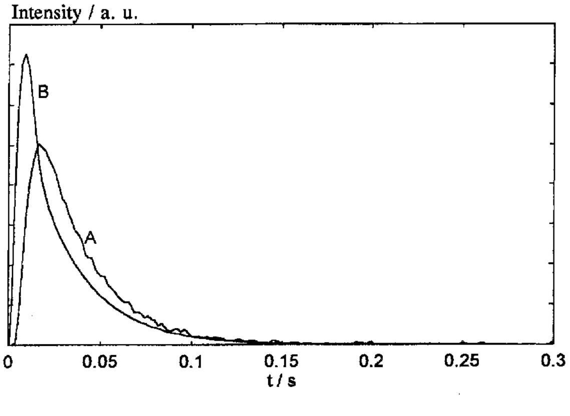

Fig. 4. Neon responses at the reactor outlet at 1013 K: (A) measured response when pulsing CH_4/Ne (1 : 1) mixture; (B) simulated response assuming that diffusion starts at the center of the catalyst bed.

A high surface residence time of hydrogen was detected in the whole range of degrees of surface reduction where hydrogen was observed. In order to clarify the reason, the adsorption of hydrogen with almost completely reduced rhodium black was investigated when H_2 conversion was negligible. From the corresponding high t_S-value, which was similar to that observed in methane conversion, can be concluded that the long mean residence time of H_2 formed in the reaction of methane is due to its strong adsorption. Most propably primary hydrogen formation by methane decomposition was realized under the conditions applied.

To analyze whether the product formation during methane interaction with the surface is affected by gas-phase oxygen the product sequence has been further investigated for the reaction of the methane/oxygen mixture with the surface. A $CH_4/O_2 = 1.8$ mixture was pulsed over Rh-black at 1013 K; the product distribution obtained after 560 pulses corresponded to complete oxygen conversion. The oxygen balance amounted to 100 ± 3% indicating that all oxygen pulsed is involved in the product formation. The responses of methane and the reaction products at the reactor outlet are presented in fig. 5; the corresponding t_S-values are summarized in table 3. Results of carbon balance indicated that carbon deposits were formed. The low yield of products containing hydrogen ($H_2O + H_2 = 68\%$) may be explained by the fact that some H_2 was not detected due to its slow desorption and/or due to formation of hydrogen-containing carbon species. Formation of CO was slower compared to other products as can be seen from the highest t_S-value (cf. table 3). Thus, its secondary formation compared to CO_2 can be assigned to the reaction of surface carbon with CO_2 according to the reaction mechanism proposed earlier [1]. Results on the reaction of surface carbon with CO_2 on Rh-black surface are described below.

Table 3
Results on yields (Y) and surface residence times (t_S) of the reaction products during pulsing of CH_4 and $CH_4/O_2 = 1.8$ mixture over Rh-black at 1013 K as well as t_S-values for the products during their separate pulsing

Products	Reaction of CH_4 after pulsing $(1.2–1.6) \times 10^{17}$ CH_4 molecules (cf. fig. 1)		Reaction of CH_4 after pulsing $(3.8–5.7) \times 10^{17}$ CH_4 molecules (cf. fig. 1)		Reaction of CH_4/O_2		Separate pulsing of reactants
	Y (%)	t_S (ms)	Y (%)	t_S (ms)	Y (%)	t_S (ms)	t_S (ms)
CO	0	–	35	113	68	67	< 1
CO_2	30	6	5	83	4	10	3
H_2	0	–	58	50	55	35	52
H_2O	26	21	15	16	13	40	n.d.

3.2.2. Interaction of CO_2 with carbon species from methane decomposition

The reaction of surface carbon species and CO_2 was found to be responsible for the formation of CO on the supported noble metal catalysts [1,17]. In order to elucidate whether the support sites are required for this reaction, the interaction of CO_2 with surface carbon on unsupported Rh was examined.

CO_2 was pulsed over Rh-black after reaction of the $CH_4/O_2 = 1.8$ mixture followed by O_2 pulsing in order to remove the remainder of carbon deposits. No conversion of CO_2 was observed in the absence of carbon deposits. Then methane (1.6×10^{16} molecules) was pulsed followed by a CO_2 pulse (0.9×10^{16} molecules) with a time interval of 0.2 s in order to examine the reaction of carbon species from methane decomposition with CO_2; the respective responses are shown in fig. 6. The formation of CO with the yield of 70% occurred during pulsing of CO_2. Results confirmed the high reactivity of carbon species from methane dissociation in the reaction with CO_2 also in the case of unsupported metal. Thus, CO can be easily formed via the reaction $C + CO_2 \rightarrow 2CO$ which appears to be the main reaction pathway of CO formation on the pure metal surfaces even without presence of support sites for CO_2 adsorption.

4. Conclusion

The mechanism of partial oxidation of methane over Rh catalysts is summarized by the following reaction sequence ($x = 1, 2, 3$):

(1) Methane activation:

$$CH_4 + 2[Rh] \rightarrow [CH_x\text{–}Rh] + ((4 - x)/2)H_2$$

$$[CH_x\text{–}Rh] \rightarrow [C\text{–}Rh] + (x/2)H_2$$

(2) Total oxidation:

$$[CH_x\text{–}Rh] + [Rh\text{–}O]$$

$$\rightarrow CO_2 + (x/2)H_2O(xOH) + 2[Rh]$$

$$H_2 + [Rh\text{–}O] \rightarrow H_2O + [Rh]$$

(3) Reversed Boudouard reaction:

$$[CH_x\text{–}Rh] + CO_2 \rightleftharpoons 2CO + (x/2)H_2 + [Rh]$$

(4) Reforming:

$$[CH_x\text{–}Rh] + H_2O/OH \rightleftharpoons CO + (x/2 + 1)H_2 + [Rh]$$

(5) Surface reoxidation:

$$[Rh] + O_2 \rightarrow [Rh\text{–}O]$$

From the results described above it follows that CH_4 interacts first with the catalyst surface leading to its dis-

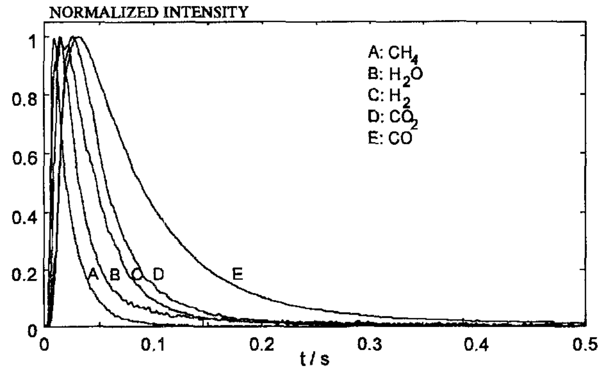

Fig. 5. Normalized responses of methane and reaction products during pulsing $CH_4/O_2 = 1.8$ mixture over Rh-black at 1013 K.

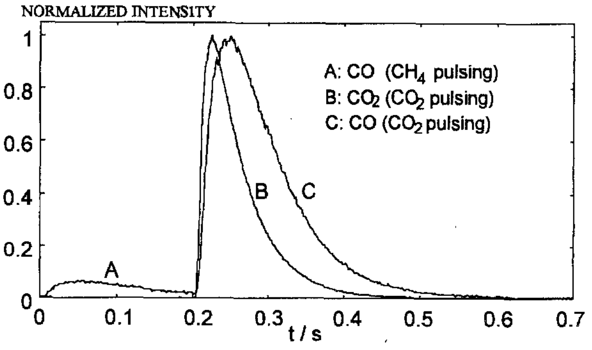

Fig. 6. Responses of CO (A and C) and CO_2 (B) in the experiment with sequential pulsing of CH_4 and CO_2 with time interval of 0.2 s over Rh-black at 1013 K.

sociation on reduced metal sites (reaction (1)); carbon species formed, in turn, react with surface oxygen yielding CO_2 (reaction (2)). A parallel reaction pathway of CO_2 formation via direct interaction of CH_4 with oxidized surface sites as proposed earlier [1] can be excluded based on the present results on Rh-black. Formation of CO occurs via surface reaction of carbon deposits with CO_2 also on Rh-black as proposed earlier for $Rh/\gamma\text{-}Al_2O_3$ (reaction (3)). No evidence for the steam reforming reaction (reaction (4)) over Rh-black was found. However, this reaction occurs on $Rh/\gamma\text{-}Al_2O_3$, as was derived from earlier DRIFTS study [3]. Comparing the reaction pathway over unsupported Rh-black with those over $Rh/\gamma\text{-}Al_2O_3$, the activity of both catalysts towards CH_4 dehydrogenation and CO_x formation was determined by the concentration of active oxygen species, i.e., by the degree of surface reduction. From the present study it was derived that Rh sites responsible for methane activation are neither related to the formation of the Rh_2O_3 nor Rh^0. Probably the partially oxidized species (Rh^+) or highly dispersed Rh^{3+} entities act as active surface centers for the dissociation of methane. For supported catalyst, such sites are stabilized by the support, which on the other side acts as a source of active oxygen involved in the consecutive oxidation of the primary reaction products (reaction (2)).

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