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Rhodium-catalyzed partial oxidation of methane to CO and H_2. In situ DRIFTS studies on surface intermediates

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Reaction steps in the oxidation of CH_4 to CO and H_2 over a Rh(1 wt%)/γ-Al_2O_3 catalyst were studied using in situ DRIFTS at 973 K and 0.1 MPa. Product distribution and the resulting absorption band intensities of the respective adsorbates were strongly influenced by oxygen coverage and carbon deposits on the surface. CH_4 is dehydrogenated to carbon deposits and H_2 and is simultaneously oxidized to CO_2 and H_2O. OH surface groups in the support are involved in the CH_x conversion to CO via reforming reaction. The reaction of surface carbon with CO_2 was assumed to contribute to CO formation. Formate is a by-product of the reaction.

Keywords: methane partial oxidation; Rh/γ-Al_2O_3; DRIFTS; surface intermediates; production of synthesis gas

1. Introduction

The discussion of the mechanism of the catalytic partial oxidation of methane to syngas is mainly based on the analysis of gas-phase kinetic data depending on the contact time and partial pressures of methane and oxygen in the catalytic fixed bed or on monoliths [1–3]. Different models were proposed including a two-step mechanism which consists of total oxidation of methane to CO_2 and subsequent reforming reactions between methane, H_2O and CO_2 [4]. The primary formation of CO and H_2 was also derived from kinetic modelling [3].

Recently, another mechanism was derived from transient pulse experiments over different supported noble metal catalysts [5]. The product distribution (CO, CO_2, H_2, H_2O) depended strongly on the surface coverage by oxygen and carbon deposits. The formation of CO proceeded with high yield via a fast reverse Boudouard reaction between carbon deposits from CH_4 decomposition and CO_2 primarily formed by total oxidation of CH_4.

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To further elucidate these mechanistic findings which were based on gas-phase reactants analysis in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) studies were applied for identification of surface intermediates from the interaction of CH_4, O_2 and CO_2 and their mixtures over a $Rh/\gamma\text{-}Al_2O_3$ catalyst. Although the temperature of 973 K applied in this study is slightly lower than proposed for process operation, the scheme derived should remain valid even when the importance of some of the steps identified may change.

2. Experimental

2.1. CATALYST

$Rh(1\ wt\%)/Al_2O_3$ ($S_{BET} = 91.4\ m^2\ g^{-1}$, $S_{Rh} = 1.1\ m^2\ g^{-1}$) was prepared by impregnating the support ($\gamma\text{-}Al_2O_3$, Degussa) previously calcined at 873 K for 14 h with an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey) to yield a nominal metal loading of 1 wt%. The impregnated powder was dried at 373 K for 2 h and subsequently reduced in a flow of H_2 at 773 K for 2 h.

Gases of commercial purity, N_2 (99.999%), CH_4 (99.95%) and H_2 (99.995%), were deoxygenated with an adsorptive oxygen trap. CO_2 (99.995%) and O_2 (99.995%) were used without further purification.

2.2. METHODS

For infrared spectroscopic measurements the catalyst powder was first treated at 973 K for 1 h in a continuous nitrogen stream (10 ml/min). For the different experiments the catalyst was either pretreated by O_2 (20 vol% O_2 in N_2) for 1 h at 973 K or reduced in H_2 (20 vol% H_2 in N_2) for 1 h at 973 K. After pretreatment with O_2 or H_2 the catalyst was purged with a continuous stream of N_2 (10 ml/min) for 30 min. Afterwards the N_2 stream was switched to the reaction gases diluted by N_2. The following reaction gas mixtures were used: 5% CH_4/N_2, 5% CH_4/5% CO_2/N_2, 5% CH_4/2.5% O_2/N_2, 10% CH_4/2.5% O_2/N_2, 10% CH_4/2.5% O_2/N_2. The total flow rate was always 10 ml/min.

For diffuse reflectance in situ IR measurements a Unicam RS FTIR spectrometer with a commercial diffuse reflectance accessory (Spectra Tech, model 003-102) was used. After pretreatment of the sample at 973 K the spectrum of the catalyst was recorded at this temperature. Then, the reaction gases were admitted until constant band intensities were observed. The spectrum of the catalyst obtained before 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. 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 being determined by the scan rate and resolution.

3. Results

3.1. INTERACTION OF CH_4 WITH THE CATALYST SURFACE

When a CH_4/N_2 stream was passed over the catalyst after treatment in pure N_2 at 973 K an absorption band at 2355 cm^{-1} was initially observed indicating CO_2 in the gas phase (fig. 1). With increasing exposure time (see second time interval of spectra recording, i.e., after 1 min) also CO was formed, while CO_2 disappeared. Both, bridged (1861 cm^{-1}) and linearly (2009 cm^{-1}) bonded CO adsorbates on Rh^0 [6] were identified. The maximum intensities of these bands were obtained after 20 min of CH_4 reaction. Another absorption band at 2169 cm^{-1} might be due to CO in the gas phase. After 40 min the CO bands had totally vanished. Simultaneously, a negative OH band at 3666 cm^{-1} was observed indicating consumption of surface OH groups in the reaction with CH_4. No CH_4 band (3014 cm^{-1}) was observed in the gas phase during the first 5 min of exposure time indicating the complete CH_4 conversion.

A band at 1597 cm^{-1}, observed immediately after CH_4 admission, was assigned to surface formate adsorbed on the Al_2O_3 support [7]. The intensity of the formate band did not depend on the exposure time.

To clarify whether carbon deposits were formed during the interaction of CH_4 with the catalyst surface, the flow of CH_4 was switched to 20% O_2/80% N_2. Only CO_2 appeared in the gas phase indicated by a band at 2353 cm^{-1}. The spectra did not reveal any CO formation.

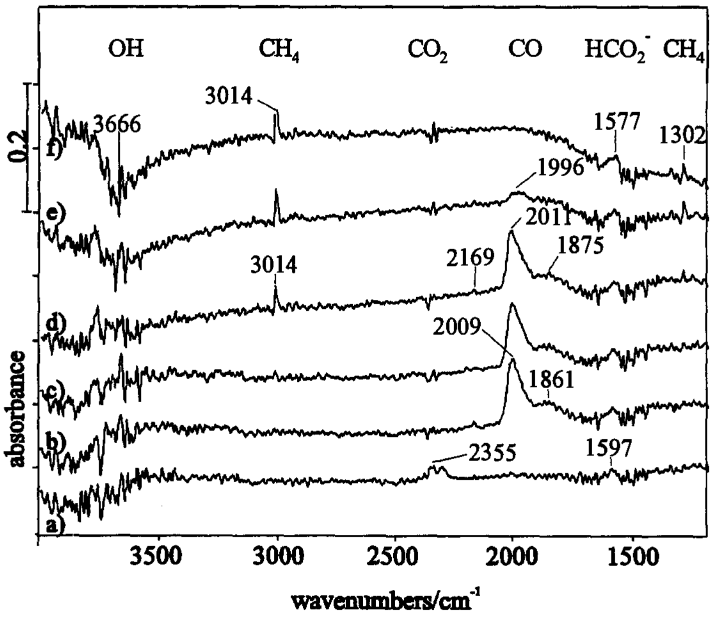

Fig. 1. DRIFTS spectra of adsorbates on the catalyst when exposed to CH_4 at 973 K after (a) 0 min, (b) 1 min, (c) 2 min, (d) 20 min, (e) 30 min, (f) 40 min.

3.2. REACTION OF CH_4 WITH O_2

The reaction of a CH_4/O_2 mixture (2 : 1) over the catalyst pretreated with CH_4 and, hence, covered by carbon deposits led to the formation of formate (1599 cm^{-1}), CO (2008, 2193 cm^{-1}), CO_2 (2333 cm^{-1}) and H_2O (3564 cm^{-1}) on the surface immediately after admitting the reaction-gas mixture (fig. 2). The band intensities of all bands remained nearly constant during the whole period of exposing the catalyst to the CH_4/O_2 mixture.

After catalyst pretreatment with O_2 the addition of the CH_4/O_2 mixture resulted in the formation of carbonate (1408 cm^{-1}), CO (1870, 2013, 2108, 2179 cm^{-1}), CO_2 (2353 cm^{-1}) and H_2O (3645 cm^{-1}) as illustrated by fig. 3. However, formate as described above was not detected. All band intensities increased during the first 5 min after exposure to the reaction mixture. This effect was not observed for the catalyst pretreated with CH_4. A slight decrease of linearly and bridged bonded CO on Rh^0 and CO_2 as well as H_2O on the surface was observed, whereas the carbonate band (1408 cm^{-1}) and the CO band at 2179 cm^{-1} remained constant. Similar results were obtained on varying the CH_4 to O_2 ratio (4 or 6). However, due to the low time resolution, changes in the initial product distribution of the reaction during the first seconds could not be observed.

3.3. INTERACTION OF CO_2 WITH THE CATALYST SURFACE

The interaction of CO_2 with Rh/Al_2O_3 was investigated over the oxidized as well as over the H_2-reduced catalyst. For the oxidized catalyst bands were assigned to carbonate (1520 cm^{-1}), while on the reduced surface neither absorption bands

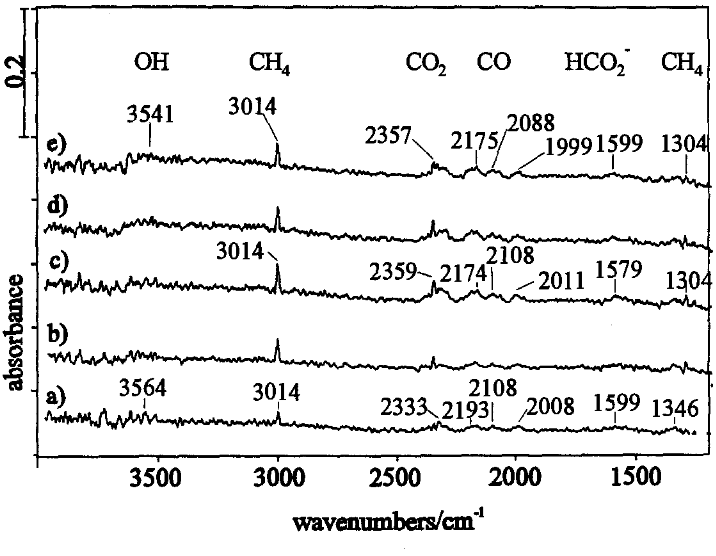

Fig. 2. DRIFTS spectra of adsorbates on the catalyst after CH_4 pretreatment at 973 K when exposed to CH_4 and O_2 (2 : 1) at 973 K after (a) 0 min, (b) 1 min, (c) 5 min, (d) 20 min, (e) 40 min.

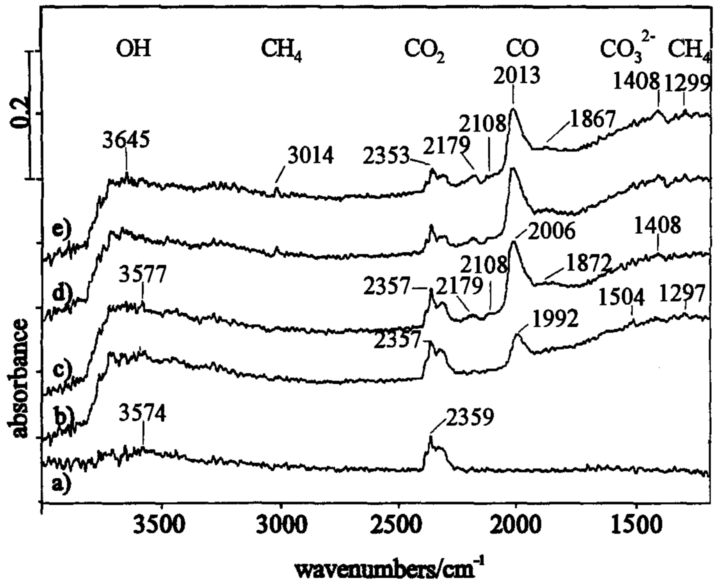

Fig. 3. DRIFTS spectra of adsorbates on the catalyst after O_2 pretreatment at 973 K when exposed to CH_4 and O_2 (2 : 1) at 973 K after (a) 0 min, (b) 1 min, (c) 5 min, (d) 20 min, (e) 40 min.

of CO_2 and carbonates, respectively, nor bands corresponding to CO formation from CO_2 dissociation were found.

3.4. REACTION OF CH_4 WITH CO_2

Passing a CH_4/CO_2 mixture (1 : 1) over the catalyst pretreated with CH_4 led to an immediate observation of CO (2000, 2183 cm^{-1}) increasing monotonously with time as illustrated in figs. 4 and 5. After 5 min the formation of a carbonate band was observed at 1409 cm^{-1}. The intensity of the CO_2 band (gas-phase and surface CO_2) passed through a maximum after approximately 5 min of exposure to CH_4.

When a CH_4/CO_2 mixture was passed over the catalyst pretreated with O_2 (fig. 6) all absorption bands revealed higher intensities. The highest CO_2 intensity was found shortly after the exposure while the band for CO passed through a maximum after approximately 1 min.

A similar effect of higher band intensities compared to the catalyst pretreated by CH_4 was also obtained for the catalyst pretreated by H_2. The time dependencies of the intensities of the CO and CO_2 bands were the same as for the catalyst pretreated by O_2 (figs. 5 and 7). Also additional formation of formate was observed.

4. Discussion

The interaction of methane with the catalyst surface indicates that the initial catalyst is active only for CO_2 formation (fig. 1) irrespective of whether its pretreatment is with oxygen or hydrogen. Hence, there should exist active sites containing

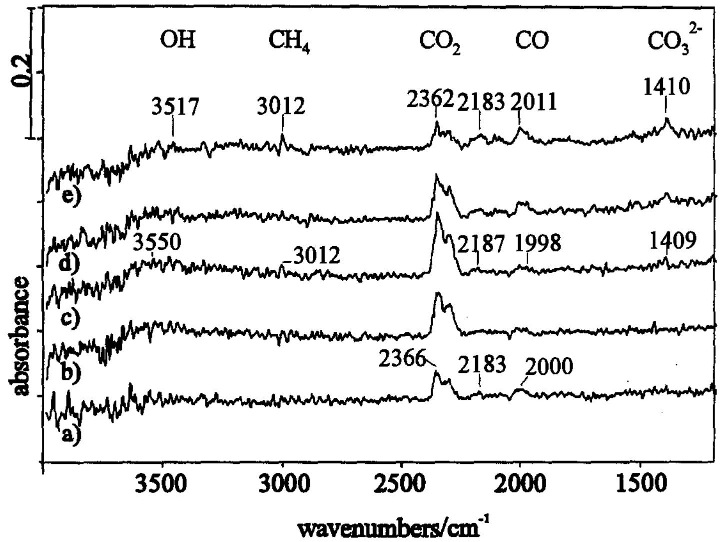

Fig. 4. DRIFTS spectra of adsorbates on the catalyst after CH_4 pretreatment at 973 K when exposed to CH_4 and CO_2 (1 : 1) at 973 K after (a) 0 min, (b) 1 min, (c) 5 min, (d) 20 min, (e) 40 min.

oxygen responsible for total oxidation even after pretreatment by H_2. The quantification by transient studies [5] of surface oxygen consumed for CH_4 oxidation resulted in a higher amount than that possibly originating from the completely oxidized bulk rhodium (Rh^{3+}). Hence, the involvement of oxygen sites of the carrier must be assumed. Simultaneously to CH_4 oxidation H_2O is most probably formed. No change in the band intensities occurred in the range from 3800 to 3400 cm^{-1} corresponding to overlapping signals of H_2O and OH groups as long as CO and CO_2 are observed as products. However, DRIFTS studies demonstrated that OH groups of the support participated in the CH_4 conversion, as it is indicated by

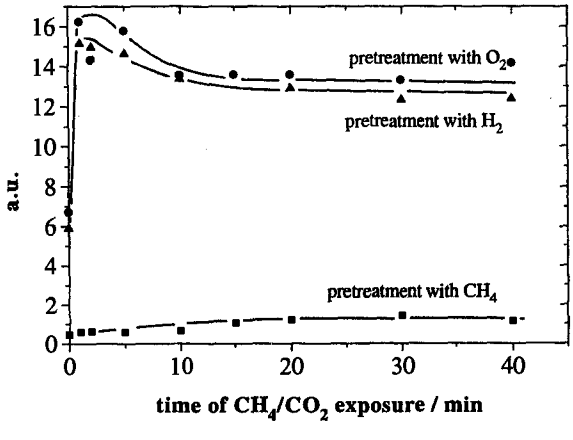

Fig. 5. Dependence of the formation of CO (intensity of absorbance bands) on the differently pretreated catalysts on time of exposure.

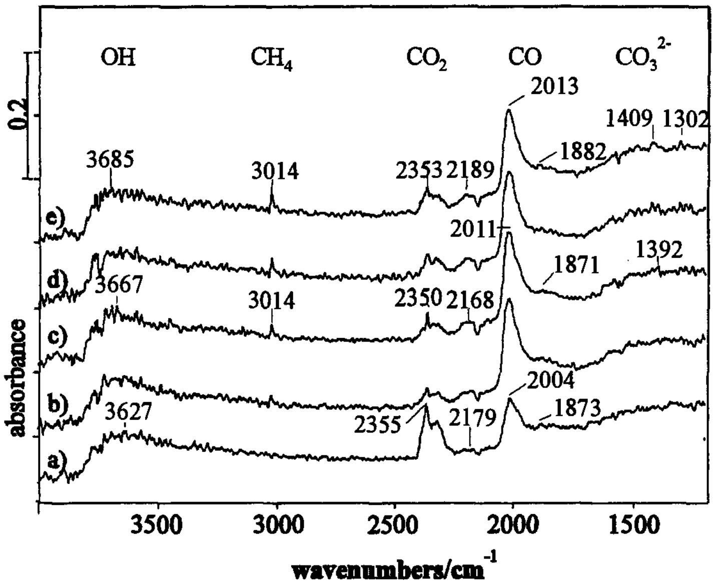

Fig. 6. DRIFTS spectra of adsorbates on the catalyst after O_2 pretreatment at 973 K when exposed to CH_4 and CO_2 (1 : 1) at 973 K after (a) 0 min, (b) 1 min, (c) 5 min, (d) 20 min, (e) 40 min.

the negative OH band after extended time of exposure. The OH species were observed independently from the pretreatment of the catalyst at 973 K (N_2-, O_2- or H_2-containing streams). This can be explained by a reforming reaction on the surface:

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

This reaction (1) resulting in CO formation should be slow compared to the total combustion of CH_4 on surface oxygen sites, since CO appeared only after extended times of exposure of CH_4 to the surface during which the degree of surface reduction probably increased. Finally, during CH_4 exposure carbon was deposited on the surface as was deduced from CO_2 formation during O_2 addition after CH_4 treatment. Although no information about the nature of the carbon species can be derived in the DRIFTS studies because identification of any CH_x species by IR spectra was impossible, the transient experiments by Buyevskaya et al. [5] revealed the existence of CH_2 species in the gas phase during the reaction of CH_4 with O_2. The fact that CO_2 was observed earlier than CO can be explained by the secondary formation of CO from CO_2 and/or the primary formation of CO_2 and CO on different sites (surface oxygen and OH groups). In the latter case CO_2 should be formed on weakly bonded oxygen species which are consumed rapidly whereas CO is formed in their absence. We cannot discriminate between these two hypotheses on the basis of DRIFTS experiments because of the low time resolution. However, the transient experiments by Buyevskaya et al. [5] clearly revealed that CO_2 is a primary product and CO is formed mainly by a fast reverse Boudouard reaction between carbon deposits and CO_2. The present studies on the reaction of CO_2 and CO_2/CH_4 mixtures with the catalyst surface support these findings. No dissociation of CO_2 forming CO was detected over differently pretreated catalyst surfaces at 973 K. However, the reaction of CH_4 with CO_2 resulted in a steady state concerning CO formation. Considering the reaction of pure CH_4 on the catalyst surface, deactivation with respect to CO formation was observed 40 min after CH_4 admission due to consumption of active oxygen and carbon deposition. Thus, steady-state formation of CO in the CH_4/CO_2 mixture can be explained by the reverse Boudouard reaction,

$$C + CO_2 \rightarrow 2CO. \tag{2}$$

To elucidate further the influence of the initial surface state of the catalyst on its final steady state in the reaction of CH_4 with CO_2, the catalyst was pretreated at 973 K in three different ways: reduction with CH_4, reduction with H_2 or oxidation with O_2. Compared to the catalysts pretreated with H_2 or O_2 formation of CO was diminished and delayed over the catalyst pretreated with CH_4 although an accelerated formation of CO was expected via reaction (2) since the reverse Boudouard reaction could start already from the beginning of CH_4/CO_2 exposure on the surface precovered by carbon deposits. The opposite finding can be explained by the decrease in activity of the carbon deposits with their extended lifetime on the surface as shown by the transient studies [5]. A different change in product distribution during CH_4/O_2 exposure was observed for the catalyst pretreated either with CH_4 or with O_2 or H_2, respectively.

During the reaction of CH_4 and CO_2 over the surface pretreated with CH_4 a maximum of the CO_2 band intensity after 5 min (fig. 7) was observed and can be interpreted as a minimum of CO_2 conversion since no active sites for CH_4 combustion to CO_2 are available after this treatment. CO_2 can be consumed only in the

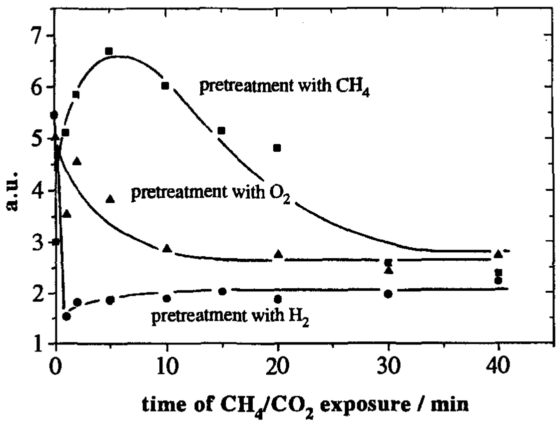

Fig. 7. Dependence of the formation of CO_2 (intensity of absorbance bands) on the differently pretreated catalysts on time of exposure.

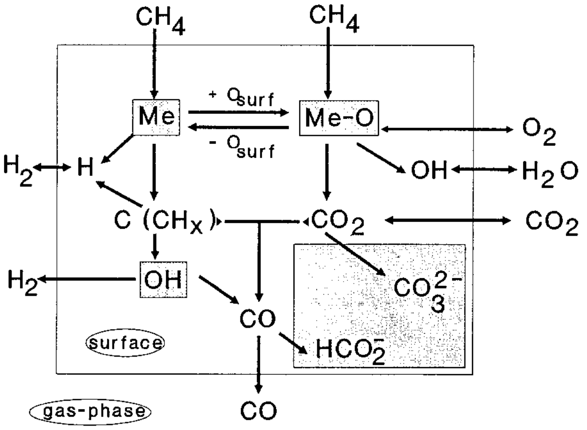

Fig. 8. Scheme of surface reaction steps in the partial oxidation of CH_4 and in CO_2 reforming methane to syngas derived from DRIFTS studies.

reverse Boudouard reaction. Since the most active CH_x species react immediately with CO_2, the average CH_x reactivity decreases during time of exposure to a mixture of CH_4/CO_2 and hence the CO_2 conversion drops. With the consumption of carbon deposits, active surface sites for CH_4 dehydrogenation are regenerated. This, in turn, leads to new active carbon deposits and increased CO_2 conversion via reaction (2).

During the reaction of CH_4 with CO_2 over the catalyst pretreated with H_2 or O_2 there was a decrease in the intensity of the CO_2 band with increasing reaction time (fig. 7). This can be related to a decrease in the catalyst activity for CO_2 production due to consumption of active lattice oxygen. An increase in the consumption of CO_2 by dissociation is rather unlikely in the absence of carbon deposits as derived from the transient and the present DRIFTS results.

In addition to CO, CO_2 and carbonate, surface species containing carbon formate were detected. Thus, the question arises how it is formed and whether it is an intermediate or a by-product. The fact that formate was not observed on oxidized surfaces reveals that additional hydrogen containing sites besides OH groups are required for its generation. An additional experiment was performed to prove the reactivity of CO_2 towards a surface reduced with H_2. No formate was formed. This result increases the likelihood that CO reacts with sites containing hydrogen (e.g. OH groups) to give formate. Generally, the intensity of the formate band did not depend on the reaction time and on the reaction gas mixture (CH_4, CH_4/CO_2, CH_4/O_2). It therefore seems that formate is a spectator rapidly formed and irreversibly bonded to the Al_2O_3 support.

5. Conclusions

Our DRIFTS results support a reaction scheme for the partial oxidation of CH_4 (fig. 8) which was derived from transient studies [5]. There is a strong dependence of the product distribution in the partial oxidation of CH_4 on the surface coverage by oxygen and carbon deposits. The mechanism of primary formation of CO_2 and its consecutive conversion in the reverse Boudouard reaction with carbon deposits to CO is confirmed. Furthermore, it was established that OH groups on the support are involved in the conversion of CH_4 although the precise mechanism of this reaction is still elusive. The observed formates are considered as spectator adsorbates in the partial oxidation of CH_4. Finally, it is important to note that a different initial coverage by oxygen and carbon deposits leads to different steady state concentrations of surface intermediates and gas-phase products.

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