The state of Rh during the partial oxidation of methane into synthesis gas

Zhijian Tian *, Olivier Dewaele and Guy B. Marin **

Laboratorium voor Petrochemische Techniek, Universiteit Gent, Krijgslaan 281 S5, Gent 9000, Belgium

Received 15 September 1998; accepted 2 December 1998

The partial oxidation of methane to synthesis gas over an α-Al_2O_3- and a γ-Al_2O_3-supported Rh catalyst has been studied at atmospheric pressure using *in situ* DRIFTS between 823 and 973 K. A surface intermediate species with IR band at 2000 cm^{-1}, correlating with the CO formation, was observed during the partial oxidation. DRIFT spectra of adsorbed CO at 323 K were used to study the state of Rh during the partial oxidation. The state of Rh at 973 K is proposed to be a matrix of metallic rhodium with clusters of partially reduced oxide phase with isolated Rh^+ atoms dispersed on the support. Rh oxide with Rh^+ cations is the state of Rh during partial oxidation of methane at 823 K.

Keywords: methane partial oxidation, synthesis gas, DRIFTS, supported Rh catalyst

1. Introduction

The partial oxidation of methane is a promising path for the production of synthesis gas, due to the more favorable H_2/CO ratio in the product gas as well as the mild exothermicity of the reaction. Transition metals are the most promising catalysts for this process [1]. The mechanism of the partial oxidation of methane to synthesis gas has been discussed in several studies. The reaction mechanism may depend on the state of the catalyst surface, as well as on the available oxygen species [2–7].

Mallens et al. [7] studied the partial oxidation of methane over rhodium sponge at 973 K in a TAP setup. Based on the comparison between experimental and simulated TAP responses, the authors concluded that CO could be formed by the direct partial oxidation of CH_4 via a Mars–van Krevelen mechanism, and that the total combustion could involve both a direct and an indirect route, depending on the type of oxygen available on the catalyst. Slaa et al. [8] studied the partial oxidation of methane over a 0.3 wt% Rh/α-Al_2O_3 catalyst in a continuous flow reactor at 1285 K. A steep increase in the oxygen conversion by increasing the space time was found on this catalyst. The corresponding product distribution shifted from CO_2 and H_2O towards CO and H_2. The authors suggested that this steep increase in oxygen conversion was accompanied by a reduction of the Rh oxide. CO_2, H_2O and C_2H_6 were found to be the primary products. Hofstad et al. [9] also observed a steep increase in conversion and change of product distribution by increasing the residence time in a TAP reactor loaded with the Rh sponge used by Mallens et al. [7] and the Rh/α-Al_2O_3 catalyst used by Slaa et al. [8] at 1123 K. Hofstad et al. [9] came to the conclusion that the primary products were dependent on the amount of surface oxygen species available, rather than on the origin of the latter, i.e., on whether a support was introduced or not. However, a support might provide an extra source of oxygen and in this manner CO_2 and H_2O were more easily formed as primary products. Wang et al. [10] also concluded that an Al_2O_3 support could act as an oxygen reservoir based on their pulse experiments at 873 K using a TAP apparatus. They proposed that the reverse spillover of OH species from the support onto the rhodium affect the activity and selectivity.

Rh/Al_2O_3 supported catalysts have been investigated extensively in the past [11–18]. Infrared spectroscopy of adsorbed CO has proven to be one of the most powerful techniques for probing the state of Rh/Al_2O_3 under reaction conditions [11–16]. The morphology and oxidation state of supported Rh can be characterized by the infrared spectra of adsorbed CO. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be very sensitive to changes of the sample surface.

The aim of the present study is to investigate the surface adsorbates (intermediates) and the surface state of rhodium during the partial oxidation of methane at temperatures as close as possible to those to be expected in industrial practice, using DRIFTS both during and immediately after reaction. The interaction of the reduced and oxidized catalyst with CH_4 and CH_4/O_2 was examined. Moreover, the behaviors of γ-Al_2O_3- and α-Al_2O_3-supported Rh catalysts, which already have been studied in the TAP reactor [9,10], were compared to investigate the effect of the support.

2. Experimental

A 0.3 wt% Rh/α-Al_2O_3 and a 0.05 wt% Rh/γ-Al_2O_3 catalyst have been investigated. The BET surface area of

---

* Permanent address: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110, Dalian 116023, PR China.

** To whom correspondence should be addressed.

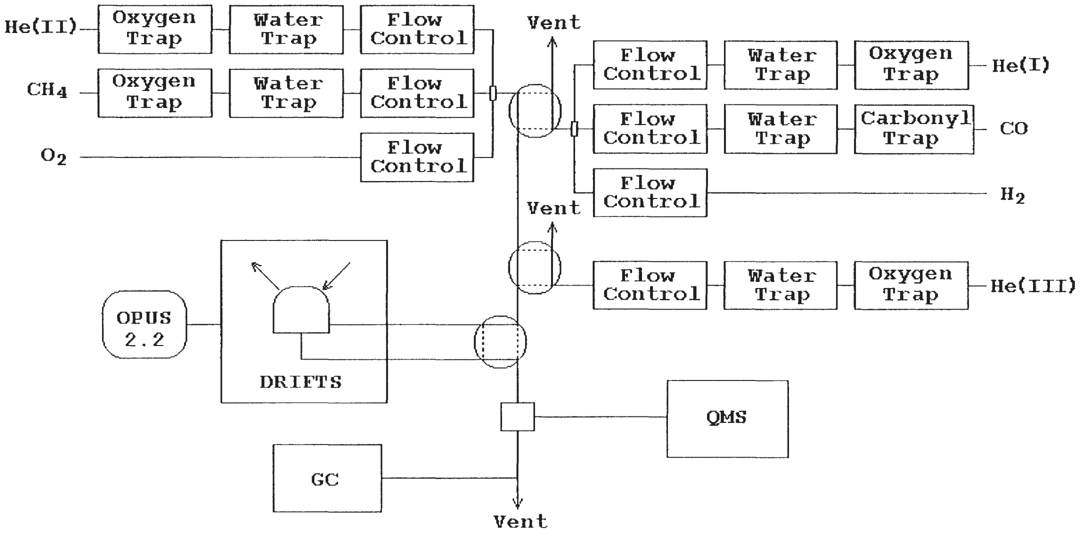


Figure 1. Schematic view of the DRIFTS set-up.

the catalysts was 0.12 and 153 m^2/g, respectively. More details of the catalyst properties can be found in [8–10]. Each catalyst sample was pretreated in the DRIFTS cell by a 20% O_2 in He mixture for 13 h and a 33% H_2 in He mixture for 5 h at 823 K to remove impurities and to obtain a stable state. Each sample was used for several experiments. No irreversible changes in the catalytic behavior occurred during these experiments.

Prior to each experiment, the catalyst was treated with the O_2/He mixture for 1 h and the H_2/He mixture for 4 h at 823 K. This resulted in a complete reduction of the Rh. The (spherical) Rh particle size was about 13 nm (H/Rh $=$ 0.081) and 81 nm (H/Rh $=$ 0.013) on Rh/γ-Al_2O_3 and Rh/α-Al_2O_3, respectively. The H/Rh ratio was determined by means of H_2 pulse chemisorption in an Altamira AMI-1 unit. The chemisorption stoichiometry was assumed to be H/Rh $=$ 1. Some reduced samples were further treated in the O_2/He mixture at 823 K for 1 h, resulting in a complete oxidation. An exposure of the reduced sample to a CH_4/He mixture at 823 or 973 K for 1 h resulted in the so-called "CH_4-exposed catalyst".

The experimental set-up is shown in figure 1. It was operated in a continuous flow mode. A Bruker Vector-22 spectrometer with a liquid nitrogen cooled MCT detector and OPUS 2.2 software was used. Typically, 0.08 g of Rh/α-Al_2O_3 or 0.04 g of Rh/γ-Al_2O_3 was placed into a cup of a high-temperature, high-pressure diffuse reflectance cell (Spectra Tech) with ZnSe windows. The cell was connected to a control unit which allowed to prepare and analyze gas mixtures at atmospheric pressure. A set of four-way valves of the control unit allowed to change the gas composition quickly. He was used as a carrier gas through lines I and II, and as a purge gas, through line III. The flow rate of He was always the same and equal to 36.0 ml/min (STP). The reactant mixtures consisted of 9.1% CH_4/He, 4.8% O_2/He and 8.7% CH_4/4.3% O_2/He. The response time to a step change of the feed gas composition was close to 10 s.

An additional purification of the commercial gases, as delivered by l'Air Liquide, was performed before feeding to the reactor cell. Helium (99.995%) and methane (99.95%) were purified in an Oxy-Trap (Alltech 8115) for O_2 removal and a molecular sieve 5 Å trap for water removal. CO (99.997%) was passed through a bed of alumina at 500 K to decompose carbonyls and through a bed of molecular sieve 5 Å at room temperature to remove water. H_2 (99.9%) and O_2 (99.995%) were used as received. The composition of the reactant mixture was controlled by a set of mass-flow controllers. All lines and valves were heated at least up to 360 K during the experiments to eliminate the adsorption of both reactants and products on the wall. A quadrupole mass spectrometer (Balzers QMG-112) was connected on-line for continuous monitoring of the reactor effluent. The mass spectrometer was equipped with a data processor (QDP 101) and home-made software, which monitored simultaneously the entire spectra and five different amu's, i.e., H_2 ($m/e = 2$), CH_4 ($m/e = 15$), CO ($m/e = 28$), O_2 ($m/e = 32$), CO_2 ($m/e = 44$). A correction was made for the contribution of CO_2 to $m/e = 28$ from its signal at $m/e = 44$. The only detected carbon-containing reaction products were CO and CO_2. The steady state was assumed to be reached when all the signals were stable. A HP GC 5880A with Porapak Q and 5A molecular sieve columns, using helium as the carrier gas and a TCD detector, was also applied for on-line gas-phase analysis. The conversion of CH_4 and selectivities to CO and CO_2 were calculated from the analysis of the outlet stream and assuming a 100% carbon balance. The CH_4 conversions on pure supports were $<0.1\%$ and $<2\%$ at 823 and 973 K, respectively. The specific activity of the catalyst was also expressed as a site time yield (STY) in units of molecules of CH_4 converted per surface Rh atom per second.

The absorbance spectra were recalculated from the reflectance spectra. A reflectance spectrum was the ratio of the single beam spectrum of a catalyst taken after or during the interaction of the catalyst with a reaction mixture, to that of a reference spectrum of the clean catalyst, taken at the same temperature in He. All spectra were the result of averaging of 30 scans with a resolution of 4 cm^{-1}. A measurement of one spectrum took less than 10 s.

The oxidized or reduced sample was flushed by He at 823 K for 10–20 min. The reaction mixture was admitted to the cell at 823 K, or after heating the sample in He to 973 K. The heating rate was 15 K/min. *In situ* DRIFTS spectra were recorded from the admission of the reaction mixture on. The minimal interval between two spectra was 13 s. The duration of each experiment was 1 h, which was long enough to obtain the steady state in most cases.

After reaction, the feed was changed to He, through line III, and the catalyst was cooled to 323 K. The cooling time from 973 to 323 K was close to 6 min. The change of the catalyst state during this process is assumed to be negligible. Exposure to a mixture of 7.6% CO/He was performed at 323 K for 6 min. The flow was switched back to He, through line III, and the DRIFTS spectra of the adsorbed CO were recorded 40 s later to determine the state of Rh. In other cases, the catalyst was flushed by pure He after reaction and exposed to a O_2/He stream at the temperature of the preceding experiment. This post-combustion experiment was performed to clarify whether carbon deposits were formed during reaction.

3. Results and discussion

3.1. Identification of the IR bands of adsorbed CO

It has been established that the predominant forms of CO chemisorbed on alumina-supported Rh are the linear form (2070–2000 cm^{-1}, coverage-dependent), the bridge form ($\sim$1850 cm^{-1}) and the gem-dicarbonyl form (doublet bands: $\sim$2090 and $\sim$2020 cm^{-1}). The first two species are associated with large metallic rhodium particles. The gem-dicarbonyl species is associated with isolated Rh^+ atoms. It is also demonstrated that, under certain conditions, a number of other minor surface species can be formed upon CO adsorption. Most of them are attributed to CO adsorption on Rh in a higher oxidation state, e.g., a band that appeared near 2100 cm^{-1} following a light oxidation of the sintered catalyst was assigned to a “monocarbonyl” Rh^+ species [13]. This assignment is based primarily on the fact that the peak is singular and blue shifted $\sim$20–40 cm^{-1} higher than that of linear CO on the reduced Rh, though there is no direct evidence that Rh is in the 1+ valence state. Moreover, a band in the range 2190–2244 cm^{-1} assigned to carbonyl groups bonded to surface Al^{3+} ions can also be observed on dehydrated alumina [15].

In order to use DRIFT spectra of adsorbed CO for the determination of the state of Rh, it is necessary to know whether CO itself can change the state of Rh at 323 K. The CO-assisted oxidative disruption of small Rh metallic crystallites at 323 K cannot be ignored [15,18–20]. However, the extent of the oxidative conversion of Rh^0 to Rh^+ is strongly dependent on the initial rhodium particle size. The larger the Rh metal particles are, the more difficult it is to disrupt them. A severe H_2 reduction (>773 K) leads to particle growth and retards the CO-assisted oxidation and disintegration of Rh particles [17]. The reductive preparation of the catalysts used here was carried out at a higher temperature (823 K). The Rh is poorly dispersed, being present in large metallic particles. Thus, the CO-assisted oxidative disruption of Rh particles at 323 K was strongly retarded. Moreover, the intrinsic low density of surface OH groups on the α-Al_2O_3 surface and the high degree of dehydroxylation of the γ-Al_2O_3 surface at the higher reduction temperature restricted the surface reaction of rhodium particles at 323 K. To summarize, the use of DRIFTS spectra of adsorbed CO for the determination of the state of Rh at 323 K is feasible on the catalysts used in the present study.

3.2. Rh/α-Al_2O_3

The DRIFTS spectrum of the adsorbed CO at 323 K over reduced Rh/α-Al_2O_3 reveals strong bands at 2068 and 1860 cm^{-1} and two weak shoulders at 2093 and 2020 cm^{-1}, as can be seen in figure 2(a) and table 1. As mentioned in the previous section, the two bands can be as-

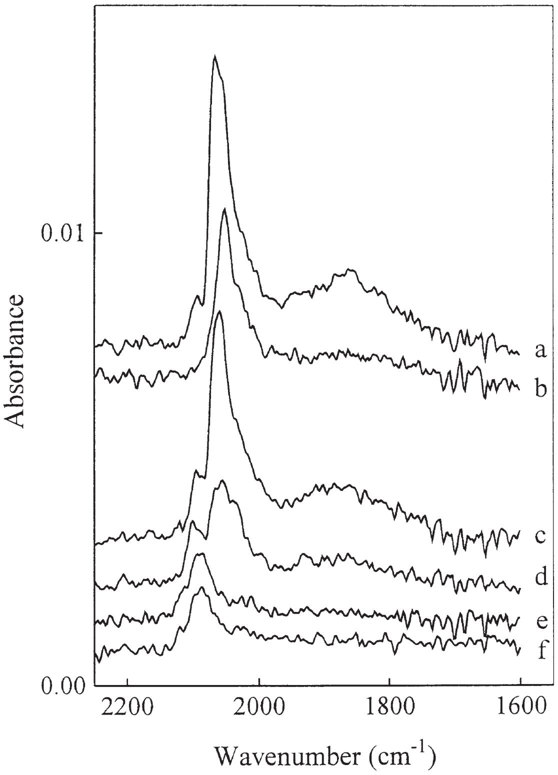


Figure 2. Spectra of adsorbed CO at 323 K on (a) reduced Rh/α-Al_2O_3; (b)* oxidized Rh/α-Al_2O_3 after 1 h CH_4 treatment at 973 K; (c)* oxidized Rh/α-Al_2O_3 after 1 h CH_4 treatment at 823 K; (d)* reduced Rh/α-Al_2O_3 after 1 h CH_4/O_2 reaction at 973 K; (e)* reduced Rh/α-Al_2O_3 after 1 h CH_4/O_2 reaction at 823 K; (f) oxidized Rh/α-Al_2O_3. * The state of the rhodium after 1 h interaction with CH_4 or reaction of CH_4/O_2 is independent of its initial oxidation state, so only a spectrum of the reduced or oxidized sample is presented here.

Table 1
Carbonyl stretching band (cm^{-1}) of adsorbed CO at 323 K.[a]

Catalyst	Linear	Bridged	Dicarbonyl	Monocarbonyl
Rh/α-Al_2O_3				
reduced	2068	1860 (b)	2093 (wsh)	–
oxidized	–	–	–	2095
Rh/γ-Al_2O_3				
reduced	2050 (nr)	–	2095, 2025	–
oxidized	–	–	2100, 2025	2100

[a] b: broad; nr: not resolved; wsh: weak shoulder.

Table 2
The ratio of the relative amount of carbon deposition on the catalyst surface after 1 h of CH_4 treatment to the number of surface rhodium atoms (normalized to the ratio on Rh/α-Al_2O_3 at 823 K).

Catalyst	823 K	973 K
Rh/α-Al_2O_3	1	3.4
Rh/γ-Al_2O_3	4.1	29

signed to linear- and bridge-bonded CO on Rh crystallites. The fact that absorption bands of the dicarbonyl species were poorly developed suggests that the Rh atoms have been completely reduced and aggregated into large particles.

The monocarbonyl Rh^+ species with absorption band at 2095 cm^{-1} in DRIFTS spectra was present on the oxidized Rh/α-Al_2O_3, as revealed in figure 2(f) and table 1. Rice et al. [13] did not determine whether this species referred to atomically dispersed Rh^+ or clusters containing some Rh^+. Because of the high aggregation of Rh atoms on Rh/α-Al_2O_3, the monocarbonyl Rh^+ species are located on Rh oxide clusters rather than atomically dispersed on the support. These Rh^+ cations are not fully oxidized, and could be considered as defects on the surface of the Rh oxide particles.

3.2.1. Interaction with CH_4

The interaction of CH_4 with oxidized and reduced Rh/α-Al_2O_3 in the absence of gas-phase oxygen, was investigated in the 823–973 K range.

After admission of CH_4/He over the oxidized Rh/α-Al_2O_3 catalyst, a transient formation of CO_2, CO and H_2 was observed by the mass spectrometer. The maximum of the CO_2 peak intensity in the mass spectrum was observed prior to that of CO and H_2. The maximum formation of all products appeared earlier with the increasing temperature. These sequences were also confirmed from the DRIFTS spectra.

No CO_2 was formed during the interaction of methane with the reduced Rh/α-Al_2O_3 catalyst in the range of 823–973 K. A transient production of H_2 and a trace of CO were observed with the mass spectrometer. No formation of carbon-containing reaction products was observed by Mallens et al. [7] on reduced Rh sponge during its interaction with CH_4. A support might, however, provide an extra source of oxygen. The effect of the support will be discussed later.

The decomposition of CH_4 terminated after about 30 s of its introduction to both the oxidized and the reduced Rh/α-Al_2O_3 catalyst. CO_2 was the only product in the post-combustion experiment of the samples after 1 h of CH_4 exposition. Carbonaceous species were, thus, deposited on the catalyst surface. The ratios of the relative amount of carbon deposition on the catalyst surface after 1 h of CH_4 treatment to the number of the surface rhodium atoms are shown in table 2. Note that the carbon deposition is not necessary limited to Rh only. Deposition on the support may be more pronounced on the γ-Al_2O_3 catalyst.

Two typical DRIFTS spectra of the adsorbed CO are shown in figure 2 (b) and (c). As compared with figure 2(a) and table 1, the DRIFTS spectra of the adsorbed CO on the CH_4-exposed Rh/α-Al_2O_3 catalyst are almost the same as that on the reduced catalyst, but relatively weak in intensity, independent of the initial oxidation state of Rh.

Apparently, methane could reduce the Rh/α-Al_2O_3 catalyst in the range of 823–973 K. Further interaction of CH_4 with the reduced Rh/α-Al_2O_3 catalyst led to carbon deposition. The carbon deposit covered the rhodium atoms and terminated the decomposition of CH_4. The abundance of surface CO species, that formed during 323 K CO adsorption, was also suppressed by the carbon deposit. It seems that the decomposition of CH_4 terminates before the surface rhodium atoms are completely covered by carbon deposit. Wang et al. [21] proposed that the methane adsorption on Rh is structure sensitive and that a limited number of Rh sites are able to adsorb methane.

3.2.2. Conversion of CH_4/O_2

As the CH_4/O_2 mixture was admitted to the reduced or oxidized Rh/α-Al_2O_3 catalyst at 823 K, a constant formation of CO_2 was observed by the mass spectrometer, as well as a transient formation of CO and H_2 which lasted nearly 300 s. A steady production of H_2, CO and CO_2 was observed on both reduced and oxidized Rh/α-Al_2O_3 samples at 973 K. The reduced and oxidized Rh/α-Al_2O_3 gave the same steady-state activity for methane oxidation in the range of 823–973 K. The experimental results at 973 K are presented in table 3.

The reaction of CH_4 and O_2 on the CH_4-exposed sample was also investigated. The carbon deposit could not be completely removed during 1 h of reaction. No CO formation was observed at 823 K. The effect of the carbon deposition was more serious at 973 K than at 823 K, because of the higher amount of carbon deposition on the surface at high temperature. The activity of methane oxidation on the CH_4-exposed catalyst was lower than those on the carbon-free catalysts, as shown in table 3.

The DRIFTS spectrum of adsorbed CO on Rh/α-Al_2O_3 after 1 h of reaction of CH_4 and O_2 at 823 K is the same as that of oxidized catalyst, independent of its initial state. A typical spectrum is shown in figure 2(e). The DRIFTS spectrum of adsorbed CO on Rh/α-Al_2O_3 after 1 h of reaction of CH_4 and O_2 at 973 K does not depend on the

Table 3
Experimental results of the partial oxidation of CH_4 on Rh/Al_2O_3 catalysts at 973 K.[a]

Catalyst	CH_4 conversion (mol%)	STY (s^{-1})	CO selectivity (mol%)
Rh/α-Al_2O_3			
oxidized	25	22	77
reduced	24	22	77
CH_4-exposed	19	17	59
Rh/γ-Al_2O_3			
oxidized	9 (18)	15 (31)	12 (58)
reduced	9 (20)	15 (34)	12 (53)
CH_4-exposed	9–10[b]	16–18[b]	3–18[b]

[a] Reactant gas-flow rate (STP): He 36.0 ml/min, CH_4 3.6 ml/min, O_2 1.8 ml/min. Pressure 1 atm. Weight of the catalyst: Rh/α-Al_2O_3 0.08 g, Rh/γ-Al_2O_3 0.04 g. The initial activities are given in parentheses.
[b] CO concentration oscillated.

initial state but is clearly different from that obtained after reaction at 823 K. Figure 2(d) gives a typical DRIFTS spectrum of the adsorbed CO after 1 h of reaction at 973 K. The band at 2103 cm^{-1} assigned to monocarbonyl Rh^+, next to the band at 2055 cm^{-1} assigned to linear-bonded CO species appears. This indicates that the catalyst surface consists of a mixture of rhodium oxide clusters and metallic crystallites. As mentioned above, the monocarbonyl Rh^+ species are believed to be located on Rh clusters rather than atomically dispersed on the support. This is in line with the absence of the doublet bands of gem-dicarbonyl species corresponding to Rh^+ atomically dispersed on the support in figure 2(d). Moreover, it should be noted that Rh cations where monocarbonyl species adsorb on are not fully oxidized but in a partially reduced state – in other words, these oxide clusters are nonstoichiometric oxide.

As a summary, it can be stated that during methane partial oxidation at 973 K Rh/α-Al_2O_3 consists of large rhodium metallic crystallites and partially reduced oxide clusters dispersed in the rhodium metal matrix, whereas at 823 K Rh oxide with a few partially reduced rhodium cations dominates the catalyst surface.

3.3. *Rh/γ-Al_2O_3*

Figure 3 shows the 2250–1900 cm^{-1} region of the spectra of adsorbed CO on Rh/γ-Al_2O_3 at 323 K. The CO absorbance below 1900 cm^{-1} is strongly masked by the presence of bands corresponding to surface carbonates.

The dominant features of the spectrum on the reduced Rh/γ-Al_2O_3 catalyst are the doublet bands near 2095 and 2025 cm^{-1} corresponding to the geminal species, as can be seen in figure 3(a) and table 1. Since these bands are not completely resolved and asymmetric, the overlap with a band around 2050 cm^{-1} corresponding to linear-bonded CO is evident. The presence of linear and dicarbonyl features in the DRIFTS spectrum suggests that the Rh/γ-Al_2O_3 catalyst contains isolated Rh atoms as well as Rh particles after the reduction. Some dicarbonyl species might be formed by oxidative disruption of small Rh metallic crystallites [15,18–20], and others were formed by truly isolated Rh^+ atoms that resisted reduction.

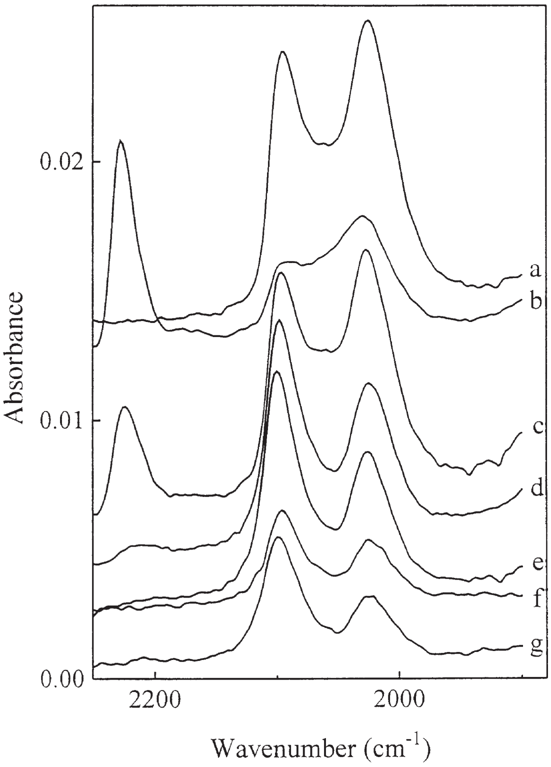


Figure 3. Spectra of adsorbed CO at 323 K on (a) reduced Rh/γ-Al_2O_3; (b)* oxidized Rh/γ-Al_2O_3 after 1 h CH_4 treatment at 973 K; (c) oxidized Rh/γ-Al_2O_3 after 1 min CH_4 treatment at 973 K; (d)* oxidized Rh/γ-Al_2O_3 after 1 h CH_4 treatment at 823 K; (e)* reduced Rh/γ-Al_2O_3 after 1 h CH_4/O_2 reaction at 973 K; (f)* reduced Rh/γ-Al_2O_3 after 1 h CH_4/O_2 reaction at 823 K; (g) oxidized Rh/γ-Al_2O_3. * The state of the rhodium after 1 h interaction with CH_4 or reaction of CH_4/O_2 is independent of its initial oxidation state, so only a spectrum of the reduced or oxidized sample is presented here.

Comparing figure 3 (g) and (a) makes it obvious that the doublet bands of adsorbed CO on the oxidized Rh/γ-Al_2O_3 are weaker in intensity than on the reduced catalyst, and asymmetric too, but with the band at 2100 cm^{-1} being more intense than that at 2025 cm^{-1}. Apparently, monocarbonyl Rh^+ and gem-dicarbonyl Rh^+ species coexist on the surface. The monocarbonyl Rh^+ species located on Rh oxide particles were present as the defects on the latter, as noted above. The gem-dicarbonyl Rh^+ isolatedly dispersed on the support.

The principal features of spectra of adsorbed CO on Rh/α-Al_2O_3 and Rh/γ-Al_2O_3 are compared in table 1. In particular, the presence of the gem-dicarbonyl Rh^+ species on the Rh/γ-Al_2O_3 catalyst suggests that the isolated Rh^+ atoms on γ-Al_2O_3 might not be oxidized fully to Rh^{3+} or reduced fully to Rh metal after oxidation and reduction at 823 K. This indicates that the aggregation of the Rh atoms on Rh/γ-Al_2O_3 is restricted because of the stronger interaction of Rh atoms with the support, as compared with Rh/α-Al_2O_3.

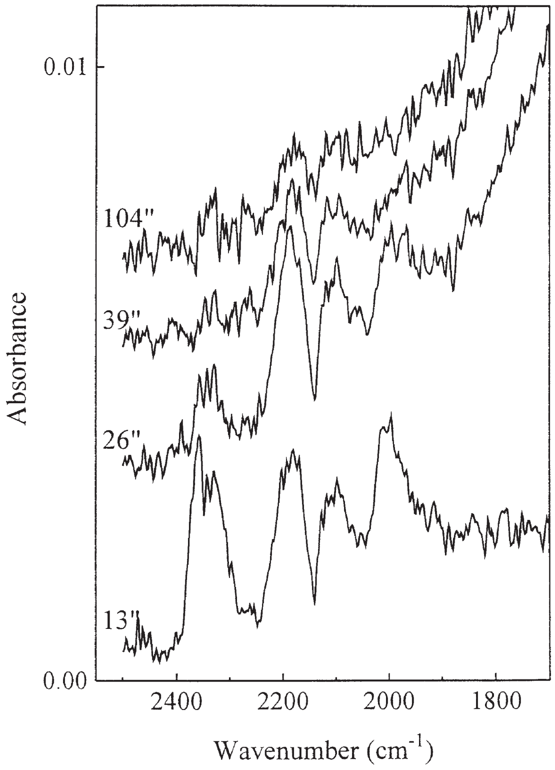


Figure 4. Spectra recorded on the oxidized Rh/γ-Al_2O_3 catalyst after CH_4 admission at 973 K.

3.3.1. *Interaction with CH_4*

The admittance of CH_4 to the reduced and the oxidized Rh/γ-Al_2O_3 between 823 and 973 K resulted in a simultaneous transient formation of CO_2, CO and H_2, as observed by the mass spectrometer. The production of CO_2 lasted nearly 60 s, while for CO about 180 s. Compared with that on Rh/α-Al_2O_3, the formation of the CO_2 and CO was more pronounced on Rh/γ-Al_2O_3.

In contrast to the Rh/α-Al_2O_3, a transient surface intermediate absorbing at 2000 cm^{-1} was observed by DRIFTS immediately after CH_4 admission, as can be seen in figure 4. The band of the surface intermediate disappeared accompanying the gradual disappearance of the bands of CO. The surface intermediate absorbing at 2000 cm^{-1} is assigned to a monocarbonyl hydride species correlating to CO formation, as will be discussed later. The absorbance intensities of the surface intermediate were stronger on the oxidized catalysts than on the reduced catalysts.

One broad negative band centered at about 3570 cm^{-1} and three sharper negative bands at 3815, 3753 and 3690 cm^{-1} developed in the DRIFTS spectra as the methane was introduced to the Rh/γ-Al_2O_3. The former band is characteristic of chemisorbed water, and the latter three bands are associated with isolated OH groups. That is, the surface OH groups were consumed during the interaction of CH_4 with the Rh/γ-Al_2O_3.

The state of Rh in the Rh/γ-Al_2O_3 catalyst established after 1 h of interaction with CH_4 was independent of the initial oxidation state. It can be found in figure 3(d) that the doublet bands after 1 h of interaction with CH_4 at 823 K are asymmetric and not resolved. A weak and multiple broad band in the 2120–1950 cm^{-1} region is present after 1 h of interaction with CH_4 at 973 K, as shown in figure 3(b). To clarify whether the Rh/γ-Al_2O_3 catalyst could be reduced by CH_4, 1 min of exposure of CH_4 to the oxidized Rh/γ-Al_2O_3 catalyst at 973 K was also performed. The result is illustrated in figure 3(c), where the spectrum after 1 min reduction of CH_4 is the same as that of the reduced Rh/γ-Al_2O_3. The situation is similar to that of Rh/α-Al_2O_3: methane reduces the Rh/α-Al_2O_3 catalyst in the range of 823–973 K, this reduction is accompanied by carbon deposition which terminates the decomposition of CH_4. The carbon deposit on the catalyst surface is also confirmed by the results of post-combustion experiments in table 2.

The band near 2220 cm^{-1} corresponding to carbonyl groups bonded to surface Al^{3+} ions in figure 3 (b)–(d) is a result of the dehydroxylation of the support.

3.3.2. *Conversion of CH_4/O_2*

The initial activity for methane partial oxidation was up to double of that shown at steady state over both reduced and oxidized Rh/γ-Al_2O_3 at 973 K. The selectivity to CO was even higher in the initial stage than that at steady state, as indicated in table 3. The initial stage lasted 600 s.

Passing the CH_4/O_2 mixture over reduced or oxidized Rh/γ-Al_2O_3 catalyst led to an immediate observation of the band at 2000 cm^{-1}, which after reaching a maximum faded away with the decreasing of CO formation. The band was weaker in intensity on the reduced sample. The DRIFTS spectra during reaction at 973 K are given in figure 5.

The band at 2000 cm^{-1} has also been observed on the Rh/α-Al_2O_3 catalyst accompanying the brief appearance of CO during CH_4/O_2 reaction at 823 K, but not at 973 K. And the intensity of the band was much less than that on the Rh/γ-Al_2O_3 catalyst.

It can be found in table 3 that the carbon deposit strongly influenced the reactivity of the Rh/γ-Al_2O_3 catalyst. After a short initial stage, the selectivity to CO on the CH_4-exposed Rh/γ-Al_2O_3 catalyst started to oscillate at 973 K. Figure 6 shows the mass spectra of outlet stream during reaction at 973 K. No formation of the surface intermediate that absorbs at 2000 cm^{-1} was observed in DRIFTS on the CH_4-exposed Rh/γ-Al_2O_3 catalyst during 1 h reaction, as well on the CH_4-exposed Rh/α-Al_2O_3 catalyst in similar condition.

During the methane oxidation, the absorption bands of surface OH groups (3815, 3735 and 3890 cm^{-1}) and chemisorbed water (3550 cm^{-1}) grew gradually due to the formation of gaseous water.

As in the case of Rh/α-Al_2O_3, the spectrum of adsorbed CO on Rh/γ-Al_2O_3 after 1 h reaction of CH_4 and O_2 at 823 K was almost the same as that of the oxidized catalyst, independent of its initial state. A typical DRIFTS spectrum of the adsorbed CO is shown in figure 3(f).

Figure 3(e) shows that the doublet bands of adsorbed CO after 1 h of reaction of CH_4 and O_2 at 973 K are asymmetric

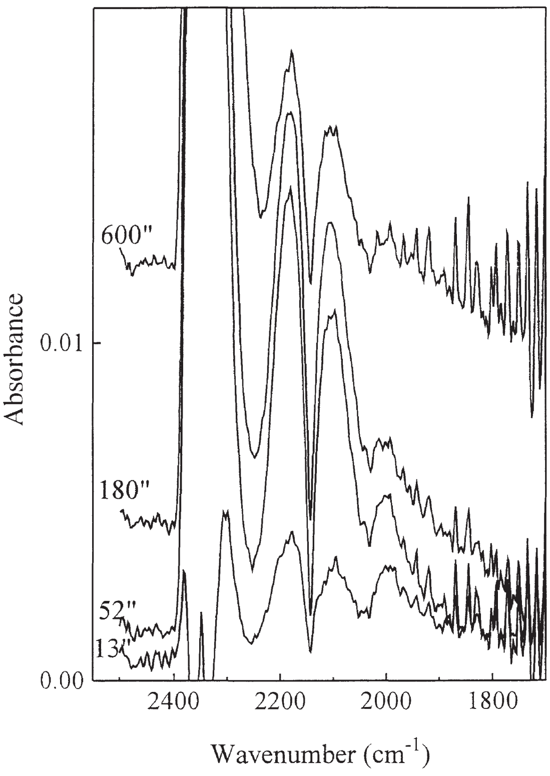


Figure 5. Spectra recorded on the oxidized Rh/γ-Al_2O_3 catalyst after CH_4/O_2 mixture admission at 973 K.

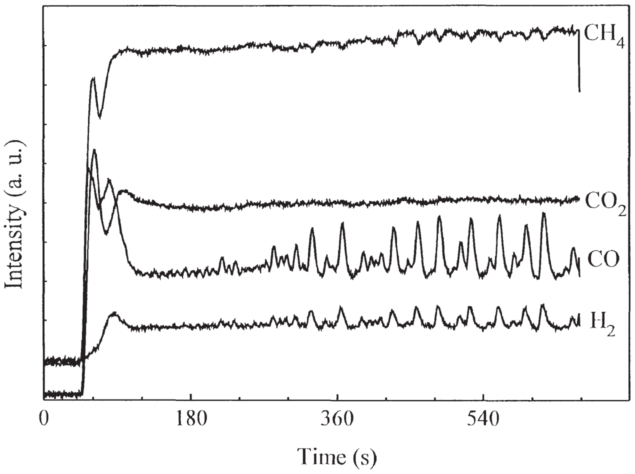
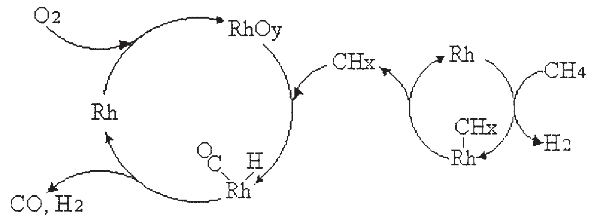


Figure 6. MS spectra of outlet stream during CH_4/O_2 reaction on CH_4-exposed Rh/γ-Al_2O_3 catalyst at 973 K.

and not resolved. By comparing figure 3(e) with figure 3 (d) and (g), it can be concluded that gem-dicarbonyl Rh^+, monocarbonyl Rh^+ and linear-bonded CO species coexist on the surface after CO adsorption. Hence, the Rh was in a partially reduced state during reaction of CH_4 and O_2 at 973 K.

In summary, during methane partial oxidation at 973 K the surface of Rh/γ-Al_2O_3 consists of rhodium metallic crystallites and partially reduced oxide clusters dispersed in the rhodium metal matrix, as well as of isolated Rh^+ atoms. At 823 K, the Rh consists of Rh oxide with partially reduced rhodium cations and isolated Rh^+ atoms are dispersed on the support.

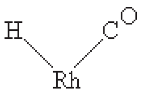


Scheme 1.

3.4. Surface intermediate species (band near 2000 cm^{-1})

The infrared band near 2000 cm^{-1} was observed during interaction of CH_4 with Rh/γ-Al_2O_3 (823, 973 K) and of CH_4/O_2 with Rh/α-Al_2O_3 (823 K) and Rh/γ-Al_2O_3 (823, 973 K). The simultaneous appearance and disappearance of the band at 2000 cm^{-1} with the bands of gaseous CO at 2143 cm^{-1} suggest that it can be attributed to a surface intermediate for CO formation, as illustrated by figures 4 and 5. The Rh/γ-Al_2O_3 catalyst was investigated in a pure CO/H_2 atmosphere between 823 and 973 K. The band near 2000 cm^{-1} was also observed. However, a rather high CO/H_2 concentration was required to obtain the same intensity as that observed during CH_4/O_2 reaction. So, the readsorption of CO and H_2 leading to carbonyl hydride is less important than its direct formation during the partial oxidation of methane.

The structure of the surface intermediate is attributed to a mono-carbonyl hydride species, shown below:



This rhodium carbonyl hydride was originally proposed by Solymosi et al. [14] as they studied the hydrogenation of CO on supported Rh catalyst.

The presence of the carbonyl hydride on the catalyst surface indicates that the surface reaction mechanism involves oxidation of an adsorbed CH_x species to form adsorbed CO and H. This may be similar to the mechanism proposed by Oh et al. [22] over alumina-supported noble-metal catalysts involving the dissociation of chemisorbed methane to adsorbed methyl or methylene radicals, the subsequent interaction of CH_x species with O adatoms forming formaldehyde, and decomposition of formaldehyde into CO and two H adatoms. However, under reaction conditions used in the present work, the surface carbonyl hydride, and not formaldehyde, is proposed as the reaction intermediate.

The carbonyl hydride intermediate was absent from the Rh/α-Al_2O_3 surface during the methane partial oxidation at 973 K. This may suggest that the lifetime of the intermediate was very short in this case, leading to concentrations below the detection limit. The rapid decomposition of the carbonyl hydride to CO avoids its consecutive oxidation to CO_2. This may be the reason for the high selectivity towards CO obtained on Rh/α-Al_2O_3 at 973 K.

3.5. Influence of the support

The influence of the support will be discussed for the experiments with methane in the absence and in the presence of gas-phase oxygen separately.

3.5.1. When feeding methane in the absence of oxygen

The interaction of CH_4 with rhodium in the absence of gaseous O_2 was strongly influenced by the support. The support can introduce an extra amount of oxygen on the catalyst surface. More CO and CO_2 were formed as CH_4 reacted with Rh/γ-Al_2O_3 than with Rh/α-Al_2O_3, due to its high density of surface OH groups on the support and high surface area, as noted in section 3.2.1.

However, the reactivity of the supported Rh catalyst is not only dependent on the amount of surface oxygen species available. It also depends on the type of oxygen available. The product sequence on the oxidized Rh/α-Al_2O_3 sample, as noted in section 3.1.1, indicates that CO_2 was the product in the reaction of methane with the fully oxidized Rh catalyst, while CO was produced on a partially reduced surface. The simultaneous initial formation of CO and CO_2 on the Rh/γ-Al_2O_3 catalyst, as mentioned in section 3.2.1, indicates that the Rh was initially partially reduced. The results from Mallens et al. [7] show that reaction of methane with chemisorbed oxygen results in a high selectivity to CO_2, whereas the reaction of methane with incorporated or nonstoichiometric oxygen leads to high selectivities to CO. In view of this, it can be assumed that a catalyst with a high selectivity for CO is a catalyst with a relative high coverage with nonstoichiometric oxygen, compared to chemisorbed oxygen. The interaction of rhodium with the support on the Rh/γ-Al_2O_3 catalyst is believed to be stronger than on the Rh/α-Al_2O_3 catalyst [23]. The reduction and oxidation of the Rh/γ-Al_2O_3 catalyst are more difficult than that of the Rh/α-Al_2O_3 catalyst, so more rhodium sites resist the reduction and oxidation and stay in a nonstoichiometric partially reduced state ($3+ > n > 0$). As a result, more nonstoichiometric oxygen species are available on the Rh/γ-Al_2O_3 catalyst. In this manner, a support may also provide different type of oxygen species on the catalyst surface, leading to the high selectivity to CO observed during the reaction of methane with the Rh/γ-Al_2O_3 catalyst.

3.5.2. When feeding both methane and oxygen

Table 3 reveals that the catalytic performance of Rh for the partial oxidation of methane, in terms of initial activity and CO selectivity, is influenced drastically by the support. An initial stage with high activity was detected on the Rh/γ-Al_2O_3, while the steady state is immediately reached on the Rh/α-Al_2O_3. The specific activity, expressed as STY, of the Rh/γ-Al_2O_3 is comparable to that of the Rh/α-Al_2O_3 at steady state, but the selectivity to CO on the Rh/γ-Al_2O_3 is remarkably low. The high initial activity on the Rh/γ-Al_2O_3 catalyst can also be caused by the extra nonstoichiometric oxygen available on the catalyst surface, explained in the previous section.

The difference in steady-state activity has a different origin. A possible explanation is that the spillover of OH groups from the γ-Al_2O_3 support to the Rh, leads to a higher amount of oxygen on the Rh, resulting in a higher selectivity to CO_2. The participation of OH groups on the support during the partial oxidation of methane has been shown by Hofstad et al. [9] and Wang et al. [21].

The influence of the support on the catalytic performance of Rh can also result directly from the interaction of rhodium with the support. The size of the Rh crystallites on the Rh/α-Al_2O_3 surface is larger than that on the Rh/γ-Al_2O_3 surface. The reduction and oxidation of little rhodium crystallites on the Rh/γ-Al_2O_3 surface is retarded, due to the strong interaction between Rh atoms with the support. Thus, the partial oxidation of methane is a more facile process on Rh/α-Al_2O_3 than on Rh/γ-Al_2O_3. More nonstoichiometric oxygen species are available on the Rh/α-Al_2O_3 catalyst during the partial oxidation of methane. So the higher selectivity to CO is obtained on the Rh/α-Al_2O_3 rather than on the Rh/γ-Al_2O_3 at steady state.

4. Conclusions

The partial oxidation of methane to synthesis gas over a Rh/α-Al_2O_3 and a Rh/γ-Al_2O_3 catalyst has been studied using *in situ* DRIFTS. The surface reaction mechanism involves oxidation of an adsorbed CH_x species to form surface carbonyl hydride which decomposes into CO and H.

The Rh state established during reaction was studied using DRIFT spectra of adsorbed CO at 323 K. The reaction temperature has a large influence on the state of Rh. During methane partial oxidation at 973 K, the surface of Rh/α-Al_2O_3 and Rh/γ-Al_2O_3 consists of rhodium metallic crystallites and partially reduced oxide clusters dispersed in the rhodium metal matrix, as well as of isolated Rh^+ atoms. At 823 K, only Rh oxide with partially reduced rhodium cations and isolated Rh^+ atoms could be observed.

The support has a large influence on the activity of Rh catalysts. Spillover of OH groups from the γ-Al_2O_3 to the Rh or a direct influence on the state of the Rh and the amount of nonstoichiometric oxygen are proposed as possible causes.

Acknowledgement

ZT thanks the Fund for Scientific Research – Flanders for a fellowship, and the Dalian Institute of Chemical Physics and the Chinese Academy of Sciences for granting a leave of absence. OD also thanks the Fund for Scientific Research – Flanders for a research fellowship. We thank Professor P.G. Menon and Dr. D.A. Bulushev for their useful discussions and assistance.

References

[1] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature 344 (1990) 319.
[2] M. Prettre, C. Eichner and M. Perrin, Trans. Faraday Soc. 42 (1946) 335.
[3] D.A. Hickman and L.D. Schmidt, AIChE J. 39 (1993) 1164.
[4] D. Dissanayake, M.P. Rosynek, K.C.C. Kharas and J.H. Lunsford, J. Catal. 132 (1991) 117.
[5] F. van Looij, E.R. Stobbe and J.W. Geus, Catal. Lett. 50 (1998) 59.
[6] O.V. Buyevskaya, D. Wolf and M. Baerns, Catal. Lett. 29 (1994) 249.
[7] E.P.J. Mallens, J.H.B.J. Hoebink and G.B. Marin, J. Catal. 167 (1997) 43.
[8] J.C. Slaa, R.J. Berger and G.B. Marin, Catal. Lett. 43 (1997) 63.
[9] K.H. Hofstad, J.H.B.J. Hoebink, A. Holmen and G.B. Marin, Catal. Today, accepted.
[10] D. Wang, O. Dewaele, A.M. De Groote and G.F. Froment, J. Catal. 159 (1996) 418.
[11] A.C. Yang and C.W. Garland, J. Phys. Chem. 61 (1957) 1504.
[12] J.T. Yates, Jr., T.M. Duncan and R.W. Vaughan, J. Chem. Phys. 71 (1979) 3908.
[13] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin and A.R. Tarrer, J. Chem. Phys. 74 (1981) 6487.
[14] F. Solymosi, I. Tombácz and M. Kocsis, J. Catal. 75 (1982) 78.
[15] M.I. Zaki, G. Kunzmann, B.C. Gates and H. Knözinger, J. Phys. Chem. 91 (1987) 1486.
[16] L. Basini and D. Sanfilippo, J. Catal. 157 (1995) 162.
[17] C. Wong and R.W. McCabe, J. Catal. 119 (1989) 47.
[18] H.F.J. van't Blik, J.B.A.D. van Zon, T. Huizinga, J.C. Vis, D.C. Koningsberger and R. Prins, J. Phys. Chem. 87 (1983) 2264.
[19] F. Solymosi and M. Pásztor, J. Phys. Chem. 89 (1985) 4789.
[20] P. Basu, D. Panayotov and J.T. Yates, Jr., J. Phys. Chem. 91 (1987) 3133.
[21] D. Wang, O. Dewaele and G.F. Froment, J. Mol. Catal., accepted.
[22] S.H. Oh, P.J. Mitchell and R.M. Siewert, J. Catal. 132 (1991) 287.
[23] H.C. Yao, H.K. Stepien and H.S. Gandhi, J. Catal. 61 (1980) 547.