

# A DRIFTS study of the stability and reactivity of adsorbed CO species on a Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with a very low metal content

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## Abstract

The paper deals with the stability and reactivity of adsorbed CO species in various atmospheres (He, O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O) on a 0.05 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined in oxygen, and uses 'in situ' diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in combination with temperature programmed reaction (TPR). The dicarbonyl Rh species, which is associated with Rh<sup>+</sup> ions, is mainly observed on the catalyst oxidized at 473–823 K or reduced by H<sub>2</sub> at 473–573 K. CO does not reduce the Rh completely to the Rh<sup>0</sup> state, even at 823 K, not because of the stabilization of Rh<sup>+</sup> ions by oxygen formed in the dissociation of CO, but mainly because of the difficulty of completely reducing Rh oxide that strongly interacts with the support. Calcination favors the stability of the dicarbonyl species. Complete reduction of the Rh proceeds in H<sub>2</sub> at 823 K. The Rh particles thus formed are not disintegrated by a joint action of CO and hydroxyl groups. The linear CO species, associated with Rh<sup>0</sup> particles, shows a higher reactivity and desorbs before the dicarbonyl species. Data on the desorption and reactivity of adsorbed CO species reveal the inhomogeneity of Rh sites. The modification of the Rh morphology during the interaction of CO with the catalyst is schematically represented. The conversion in the CO methanation reaction decreases simultaneously with the intensity of the band corresponding to the dicarbonyl species. The presence of the dicarbonyl species reflects the sintering process of metallic Rh in this reaction. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* DRIFTS; Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; CO

## 1. Introduction

Rhodium is used as a component of heterogeneous catalysts for automotive emission control, CO hydrogenation and partial oxidation of natural gas. Since Ni catalysts used so far in these

processes are very sensitive to carbon formation Rh catalysts have recently received considerable attention, in spite of their low availability and high cost.

The temperature of calcination of Rh oxide supported on alumina strongly influences its interaction with the support and consequently the reactivity of the catalyst [1–5]. Rh-catalysts can be divided into two groups, depending on the calcination. The first group consists of catalysts, which have not undergone too severe

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oxygen treatments. Catalysts calcined in oxygen at temperatures higher than 773 K form the second group. High oxidation temperatures favor the diffusion leading to well dispersed Rh oxide and to a strong interaction with the alumina support of Rh oxide particles caught into defect sites on the alumina surface [1–5]. This is the main reason for the difficulty of the reduction of Rh oxide in such samples [1–5].

According to IR studies, three main states of adsorbed CO can be obtained on supported Rh catalysts. Linear and bridged forms correspond to the adsorption of CO on Rh particles or clusters in the zero oxidation state and are observed also on bulk metallic catalysts. Two CO molecules can be linked to one positively charged Rh atom, forming the geminal dicarbonyl Rh species,  $\text{Rh}(\text{CO})_2$ . Its nature and mechanism of formation were studied in detail on reduced catalysts which had not undergone a high temperature oxidation [6–14]. These studies showed that the Rh in the dicarbonyl species is in the atomically dispersed state. The rupture of the Rh–Rh bond in a crystallite of Rh is more likely than that of the Rh–CO bond because its energy is lower than that of the latter [7]. Van't Blik et al. [7] suggested that dissociation of CO and the subsequent oxidation of  $\text{Rh}^0$  by adsorbed oxygen are responsible for the formation of  $\text{Rh}^{1+}$ . Basu et al. [8] and Solymosi and Knozinger [13] deny this route because dissociation of CO proceeds at temperatures higher than 440 K, whereas the oxidative disruption of Rh crystallites occurs at room and lower temperatures. They assumed that hydroxyl groups from the support oxidize the isolated Rh atoms. Correlation between the attenuation of hydroxyl bands and the growth of the bands of the dicarbonyl species was observed [8,12]. It is interesting that at temperatures above 423 K the effect of CO on the structure of Rh is reversed. CO is responsible for the agglomeration of Rh to metallic crystallites [9,13,14]. The first direct visual evidence of processes of disintegration and agglomeration of Rh particles induced by CO was obtained recently by means of

scanning tunneling microscopy for Rh/ $\text{TiO}_2$  catalysts [15].

Temperature programmed desorption of CO from supported Rh catalysts leads to one [16] or several CO peaks [17]. Carbon dioxide, hydrogen and methane have also been observed in the thermal desorption spectrum [16,17]. The formation of the latter products was explained by the Boudouard reaction [17] and by reaction of adsorbed CO with hydroxyl groups of the support [16,17]. The stability of the Rh dicarbonyl species is considered to be lower than that of the linear and bridged CO species [6,12]. However, quite mild  $\text{O}_2$  treatment at 673 K for 10 s before CO adsorption resulted in an opposite order for the stability of CO species [18]. It was also reported, that some fraction of the dicarbonyl species can be removed only at 573 K [13,19] and even that they can survive for a long time at that temperature [20].

The dicarbonyl species is considered as a spectator in CO oxidation and hydrogenation reactions, because its reactivity is lower than the reactivity of the linear and bridged adsorbed CO [21–23]. Yet, a reverse order of reactivity with respect to  $\text{O}_2$  and  $\text{H}_2$  was also reported [24].

The state of Rh and its morphology can determine the catalytic activity and the selectivity of the process. A stronger metal-support interaction at extremely low concentration of Rh which can provide the change of catalytic properties can be expected. Thus, a control of the state of the metal is very important. Insufficient sensitivity of the several techniques does not allow to perform the Rh characterization in very diluted samples. The possibility of application of in situ FTIRS especially at high temperatures close to ones used for the partial oxidation and reforming of natural gas makes it a very important technique for the study of the state of Rh. It was shown that FTIRS is sensitive enough to detect CO adsorption on the Rh/ $\text{Al}_2\text{O}_3$  catalyst containing only 0.005% of Rh [25]. However, interaction of CO with catalysts with a Rh content lower than 0.2% have not been studied by FTIRS in detail.

The objective of the present paper is to investigate the stability of adsorbed CO species on a calcined Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with a very low Rh content by means of DRIFTS and TPR, to study their reactivity with respect to steam, H<sub>2</sub> and O<sub>2</sub>, and to compare the results with those obtained on an uncalcined catalyst with higher Rh content, reported in the literature.

## 2. Experimental

The 0.05 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the same as the one used earlier for the TAP reactor study of the methane oxidation [26]. A  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a BET surface area 153 m<sup>2</sup>/g was impregnated by RhCl<sub>3</sub> · 3H<sub>2</sub>O and the sample thus obtained was calcined at 813 K in air for 6 h. An EDX analysis revealed the presence of approximately 0.8 wt.% Ti, 0.4 wt.% Na and 0.3 wt.% of K. An ESCA study of the sample did not detect any Rh present because of insufficient sensitivity.

Prior to the experiments the sample was treated in a DRIFT cell by an O<sub>2</sub>/He mixture for 6 h, followed by a H<sub>2</sub>/He mixture for 0.5 h at 823 K. Such treatment completely removes chlorine from the sample. Gas compositions corresponded to 8.3 vol.% O<sub>2</sub>/91.7 vol.% He and 14.3 vol.% H<sub>2</sub>/85.7 vol.% He. Cleaning of the sample after an interaction with CO included a treatment by the O<sub>2</sub>/He mixture at 823 K for 3 h. Several samples of the catalyst were studied. The inertness of the support with respect to the formation of adsorbed CO species was carefully checked. The support was also inert in the CO hydrogenation reaction.

The experiments were carried out in a Bruker Vector-22 spectrometer with a MCT detector, with on-line DRIFT cell and OPUS 2.2 software. 0.03 g of the crushed Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was placed into the cup of a high temperature diffuse reflectance cell (Spectra Tech 003-102) with ZnSe windows [27]. The tip of a thermocouple was inserted into the center of the catalyst layer. The atmosphere of the compartment

surrounding the cell was purged with dry air to eliminate H<sub>2</sub>O and CO<sub>2</sub>. The cell is connected with a control unit which allows to prepare and analyze gas mixtures at a pressure close to 101 kPa. All lines and valves were heated to at least 360 K during the experiments. The composition of the reaction mixture was controlled by a set of mass-flow controllers. An additional purification of the commercial gases was performed, as explained in Ref. [27]. The flow rate of He was always the same and equal to 40.8 ml/min STP. Water was introduced to an evaporator by means of a syringe-pump. A Balzers QMG-112 mass-spectrometer and a HP5880 gas chromatograph were used for the gas phase analysis.

The absorbance spectra presented are recalculated from the reflectance spectra. A reflectance spectrum is the ratio of a single beam spectrum of the catalyst taken after or during the interaction of the catalyst with CO, to that of a reference spectrum of the oxidized catalyst, taken at the same temperature in He. The spectra are the result of averaging 30 scans with a resolution of 4 cm<sup>-1</sup>. The measurement of one spectrum took 10 s. The interaction of a 11.6 vol.% CO/88.4 vol.% He mixture with the catalyst was performed until no noticeable change was observed in the spectra (normally 20–40 min). DRIFTS measurements were performed every 50 K in the TPR experiments, or after 0.5 min during adsorption and reactivity studies. The heating and cooling rates amounted to 15 K/min.

## 3. Results and discussion

### 3.1. Interaction of CO with the reduced catalyst

The interaction of CO with the catalyst reduced in H<sub>2</sub> at 823 K caused the formation of a single adsorbed CO species, which is characterized by the band around 2040 cm<sup>-1</sup> (Fig. 1 a,b). This species corresponds to the linear CO adsorbed species, which is associated with the presence of Rh crystallites or clusters in the zero oxidation state. Thus, the reduction of the

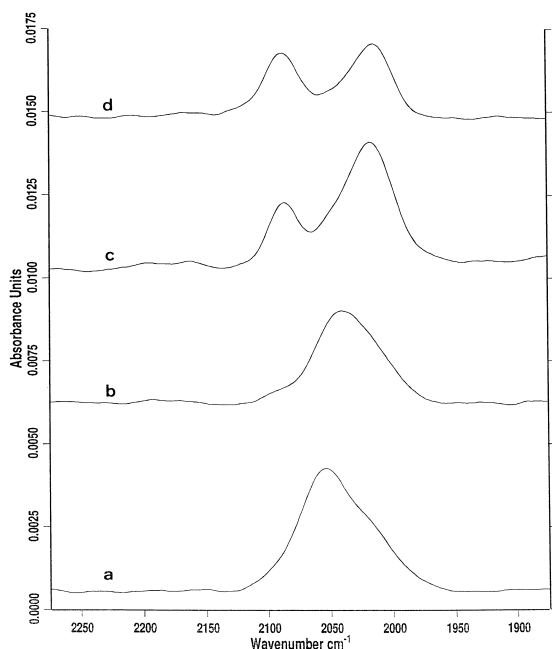


Fig. 1. Spectra of the catalyst in He after the adsorption of CO at 320 K (a) and 423 K (b–d) for 40 min. Pretreatments: (a,b) H<sub>2</sub>, 823 K, 30 min, (c) H<sub>2</sub>, 823 K, 30 min; CO, 423 K, 30 min; O<sub>2</sub>, 473 K, 15 min, d) O<sub>2</sub>, 823 K, 120 min; H<sub>2</sub>, 473 K, 30 min.

supported Rh oxide by H<sub>2</sub> is complete at 823 K. Subsequent adsorption of CO for 40 min does not result in the formation of the dicarbonyl Rh species, accompanied by the disintegration of Rh crystallites, neither at 320 K (Fig. 1a), nor at 423 K (Fig. 1b).

As shown previously for samples with a larger Rh content [9,28,29] undergone the reduction at even higher temperature disintegration of Rh particles accompanied by the formation of the dicarbonyl species is observed during the period of time of CO interaction used at the present

work. For the sample studied the dicarbonyl species was not revealed even after removal of the less stable and more reactive linear species (Table 1).

After the consecutive introduction of O<sub>2</sub> on the catalyst containing the linear CO species and metallic Rh particles a complete removal of adsorbed CO species was observed in the temperature range 423–473 K. A repeated interaction of CO at 423 K with such oxidized catalyst caused the appearance in the spectrum of twin bands of the dicarbonyl Rh species (2086, 2017 cm<sup>-1</sup>) (Fig. 1c), and the band of the linear species, although weaker than in Fig. 1b. The presence of the linear species was shown in the difference spectrum after heating the catalyst and/or interaction with hydrogen or oxygen.

The Rh in the dicarbonyl species is in the atomically dispersed state [6–14], so that the presence of the dicarbonyl species points out that a disintegration of Rh particles takes place, even at quite moderate temperatures of oxidation (473 K). CO is not able to reduce Rh completely to the zero oxidation state under these conditions. Even H<sub>2</sub> at 473 K cannot achieve this. An interaction of CO with the catalyst reduced by H<sub>2</sub> at 473 K is mainly accompanied by the formation of the dicarbonyl species (Fig. 1d). The spectrum of CO adsorbed on the catalyst reduced at 573 K in H<sub>2</sub> was very much the same.

At moderate temperatures (473–573 K) H<sub>2</sub> is known to completely reduce Rh into the zero oxidation state in uncalcined and bulk Rh samples [12,14,17]. This is not the case for the

Table 1

Stability of the adsorbed CO species formed during the interaction of a 11.6 vol.% CO/88.4 vol.% He mixture with the Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 423 K

| Gas-phase composition                    | Temperature of maximum rate of decomposition of the dicarbonyl species (K) | Temperature of maximum rate of removal of the linear species (K) |
|--|--|--|
| He                                       | 623–673  | 473–523  |
| 8.3 vol.% O <sub>2</sub> /91.7 vol.% He  | 523–573  | 423  |
| 14.3 vol.% H <sub>2</sub> /85.7 vol.% He | 573–623  | 423  |
| 7.4 vol.% H <sub>2</sub> O/92.6 vol.% He | 423  | 423  |

sample studied however. Neither  $H_2$  nor CO at moderate temperatures can completely reduce the catalyst. They transform Rh mainly into the  $Rh^+$  state. The intensity of the band corresponding to the linear CO species was stable during the interaction of CO, but the intensity of the dicarbonyl species increased slowly with time. The difficulty of reducing Rh was noticed previously for Rh/ $Al_2O_3$  catalysts calcined in air at temperatures higher than 773 K [1–4]. Such a treatment is responsible for the formation of dispersed Rh oxide species which strongly interact with alumina and are not easily reduced [1,4]. According to Ref. [4] these dispersed oxide species occupy the defect sites in the alumina surface layer.

### 3.2. Interaction of CO with the oxidized catalyst

Only the dicarbonyl species in low concentration is observed during the interaction of CO at 320 K with the oxidized catalyst (Fig. 2a). At this temperature the largest oxide particles are

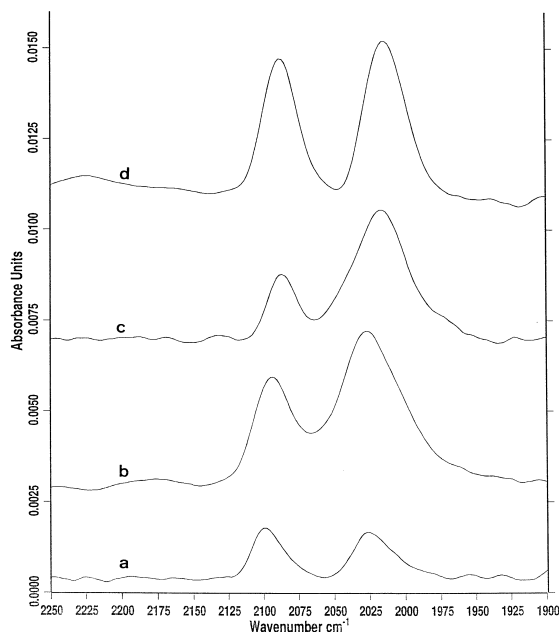


Fig. 2. Spectra of the catalyst in He (a, b, c) and in CO (d, gas phase CO is subtracted). Temperature of CO interaction and measurement: 320 K (a), 423 K (b), 573 K (c) and 823 K (d). Catalyst was first oxidized before every run at 823 K.

reduced first into the  $Rh^+$  state, but not to  $Rh^0$ . The linear species is obtained at higher temperatures. The formation of the dicarbonyl species is fast during the first 2 min at 423 K, after which it slows down. The intensity of the band of the linear species does not change any more after 2 min at this temperature. The band of gas phase CO was subtracted from the spectrum at 823 K, since the dicarbonyl species is in equilibrium with gas phase CO.

The band of the linear species is strongest at 573 K and it shifts to a lower wavenumber with rising temperature, in accordance with [18]. The ratio of  $Rh^0/Rh^+$  is lower at 423 K than at 573 K because of the slower rate of reduction. It can be higher at 823 K but the linear CO species is present in low concentration only, because of its low stability (Table 1). In the presence of gas phase CO the bands of the dicarbonyl species become stronger with rising temperature in the range 573–823 K. This is explained by the reduction of the dispersed Rh oxide species to the  $Rh^+$  state by CO, a reaction which proceeds only at temperatures higher than that required for the reduction of the bulk Rh oxide.

Heating the catalyst to 823 K in He and repeated interaction of CO at 423 K produced a spectrum identical to that observed after the first interaction. The consecutive treatment of the catalyst by CO at 423 K during 16 h did not change the spectrum. This observation differs from these made in previous studies on uncalcined catalysts with higher Rh content [13,14,18] where important changes of the Rh state in time in the presence of CO were observed. The present data show that the mobility of the dicarbonyl species is much lower in the catalyst studied here.

The interaction of CO with the sample reduced by  $H_2$  at 823 K leads to the linear CO species on the metallic particles (Fig. 1a,b), while the dicarbonyl species involving the dispersed  $Rh^+$  ions dominates in the sample reduced at 473 K (Fig. 1d) or at 573 K, as well as on the oxidized catalyst (Fig. 2). The formation of the dicarbonyl species on uncalcined samples

results from the joint action of CO and hydroxyl groups on metallic particles [7,8,12]. The formation of the dicarbonyl species does not proceed according to this mechanism on the catalyst studied here (Fig. 1a,b). It is doubtful that H<sub>2</sub> would reduce all Rh to the metallic state at 473 K, followed by disintegration of the metallic particles upon CO adsorption. The temperature used for the adsorption of CO (423 K) is not favorable for such disintegration and no dynamic features supporting this were observed in the present study.

### 3.3. Influence of steam and hydroxyl groups on the interaction of CO with the catalyst

During the reduction by H<sub>2</sub> at 473 K hydroxyl groups are kept on the catalyst in a higher concentration than on the catalyst reduced at 823 K, so that they can participate in the dicarbonyl formation. The following observations seem to reject this, however. The bands in the hydroxyl region were quite intensive in a single beam spectrum, even in the experiments at 823 K. This temperature is not sufficient for a complete removal of hydroxyl groups from an alumina surface [30]. A total concentration of hydroxyl groups at 823 K can be supposed to be of the order of 10<sup>18</sup> OH/(m<sup>2</sup> Al<sub>2</sub>O<sub>3</sub>) [30,31]. A complete reduction of Rh oxide by H<sub>2</sub> cannot provide a noticeable change of the hydroxyl group concentration. The change would be of the order of 3.10<sup>16</sup> OH/(m<sup>2</sup> Al<sub>2</sub>O<sub>3</sub>).

Experiments on the interaction of steam with the catalyst containing two forms of adsorbed CO showed the removal of the main part of adsorbed CO species at 423 K (Fig. 3). A certain fraction of the dicarbonyl species did not interact with the steam. An increase of the steam partial pressure did not change the intensity of the CO adsorbed bands, only the water bands became more intensive. The removal of the main part of adsorbed CO in a steam flow (Fig. 3) can be explained by the occurrence of the water–gas shift reaction, as proposed by Zaki et al. [12]. The treatment of the catalyst by

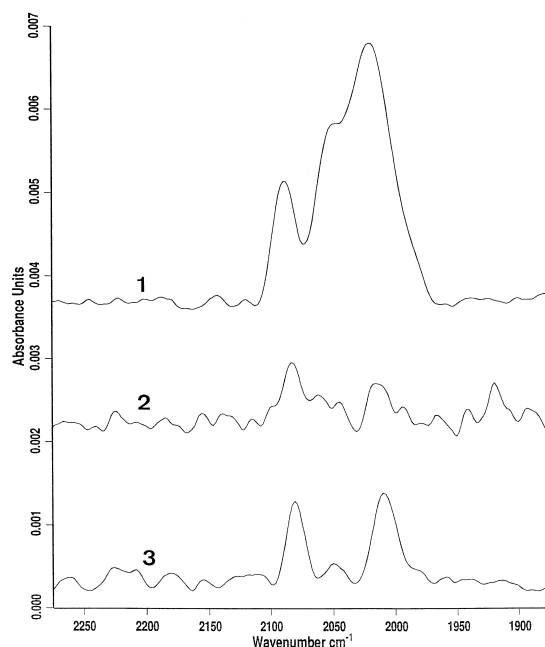


Fig. 3. Spectra of the region of adsorbed CO at 423 K. (1) After interaction of a feed consisting of 11.6 vol.% CO/88.4 vol.% He at 573 K with the catalyst oxidized at 823 K, (2) after (1), during the admission of steam (3.7 vol.% H<sub>2</sub>O/96.3 vol.% He), (3) after (2), and a subsequent treatment by a 10.7 vol.% CO/6.6 vol.% H<sub>2</sub>O/82.7 vol.% He mixture for 23 min, by a 11.6 vol.% CO/88.4 vol.% He mixture for 15 min and He for 30 min.

a CO/H<sub>2</sub>O mixture did not cause a substantial increase of the concentration of adsorbed CO. The previous level of the concentration was not reached in a CO flow even after interrupting the steam flow (Fig. 3). The influence of steam on the amount of adsorbed CO at 573 K was completely identical. The dicarbonyl species were only partially removed, reflecting the existence of different varieties of the dicarbonyl species, one of which is very reactive with respect to steam. From desorption studies Dictor and Roberts [18] suggested the presence of more than one Rh dicarbonyl species which are indistinguishable spectroscopically. Solymosi and Knozinger [13] reported that some fraction of the dicarbonyl species can hardly be removed at 573 K, while another fraction can be removed at 423–473 K. The existence of two different dicarbonyl species was derived from <sup>13</sup>C-NMR studies [10]. The first type is an isolated Rh

dicarbonyl species, the other is clustered. The latter sites are paramagnetic Rh particles surrounded by the dicarbonyl species.

Dictor and Roberts [18] suggested that steam increases the mobility of  $\text{Rh}^+$  species, leading to the formation of metallic particles at 423 K. This could occur for the catalyst studied here too, but only at a temperature of 823 K, which is much higher than the one used by Dictor and Roberts. In the present work the dicarbonyl species only slowly disappeared in a  $\text{CO}/\text{H}_2\text{O}$  mixture at 823 K from the oxidized catalyst, probably because of transformation of the  $\text{Rh}^+$  to the metallic state. This was not observed during the interaction of CO with the oxidized catalyst and in the absence of steam. The removal of the dicarbonyl species may also be ascribed to  $\text{H}_2$  formed in the water–gas shift reaction. The experiments with the introduction of steam in the  $\text{CO}/\text{He}$  flow did not support the point of view that the absence of the dicarbonyl species on the catalyst reduced by  $\text{H}_2$  at 823 K can be explained by a concentration of hydroxyl groups which is lower than that after reduction at 473 K.

### 3.4. Influence of oxygen on the interaction of CO with the catalyst

To check the probability that adsorbed oxygen formed from the dissociation of CO is the cause of the difficulty of completely reducing the Rh by means of CO the following ‘in situ’ DRIFTS experiments were performed. The catalyst was reduced by  $\text{H}_2$  at 823 K, so as to form Rh crystallites in the zero oxidation state. After this, CO was fed to the reactor for up to 23 min and also at 823 K (Fig. 4). The dicarbonyl species was not detected. Only a very weak band of the linear species was observed. Thus, even if dissociation of CO cannot be rejected from these experiments, the modification of the Rh state by oxygen formed in this process does not occur to a measurable degree.

Dicarbonyl species are observed when  $\text{O}_2$  is added to CO. Their concentration rises slowly

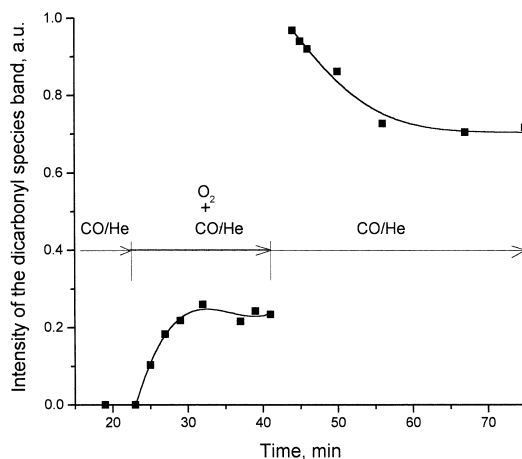


Fig. 4. Effect of the  $\text{O}_2$  addition to a  $\text{CO}/\text{He}$  stream at 823 K on the intensity of the band of the dicarbonyl species at  $2017\text{ cm}^{-1}$ . Compositions of the feeds: 11.6 vol.%  $\text{CO}/88.4\text{ vol.}\% \text{ He}$  and 10.7 vol.%  $\text{CO}/7.4\text{ vol.}\% \text{ O}_2/81.9\text{ vol.}\% \text{ He}$ . The catalyst was first reduced by a 14.3 vol.%  $\text{H}_2/85.7\text{ vol.}\% \text{ He}$  mixture at 823 K.

with time and steady-state is reached (Fig. 4, from 23 to 41 min). This rise can be explained by the transformation of a fraction of  $\text{Rh}^0$  sites into  $\text{Rh}^+$  and into  $\text{Rh}^{3+}$  (Fig. 5). The role of  $\text{O}_2$  in the formation of the dicarbonyl species has already been reported [18,20,32]. Metallic particles are disintegrated partially by oxygen in the presence of CO (Fig. 5). The smallest Rh particles are more easily oxidized than the large ones [33], leading to the dispersed Rh oxide species and  $\text{Rh}^+$  ions. The low concentration of Rh in the sample ( $2 \cdot 10^{16}$  atoms/ $\text{m}^2 \text{ Al}_2\text{O}_3$ ) allows it to occupy some specific sites on the strongly heterogeneous alumina support [34].

Interruption of the  $\text{O}_2$  flow in the  $\text{CO}/\text{O}_2$  feed mixture did not cause a decomposition of the dicarbonyl species and the catalyst did not return to the state corresponding to that in the original CO-feed. In addition, the intensity of the bands of the dicarbonyl species rapidly increased before slowly decreasing to the steady-state value (Fig. 4, from 44 min onwards). This behavior cannot be explained by the change of the CO partial pressure. CO reduces the dispersed Rh oxide species to the  $\text{Rh}^+$  state after the stop of the  $\text{O}_2$  flow. The maximum concen-

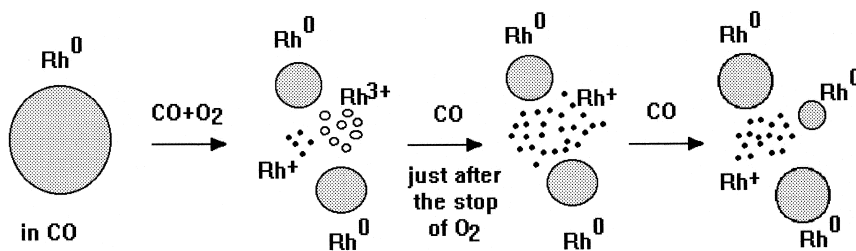


Fig. 5. Modification of rhodium morphology in the experiment presented in Fig. 4.

tration of the dicarbonyl species reached after 44 min probably corresponds to a state whereby  $\text{Rh}^{3+}$  species are absent (Fig. 5). The subsequent decrease of the concentration of the dicarbonyl species and  $\text{Rh}^+$  ions (Fig. 4) proceeds because of the growth of metal crystallites and/or the appearance of new metallic particles (Fig. 5).

The bridged adsorbed CO species is known to give a broad band at  $1870\text{--}1820\text{ cm}^{-1}$ . This species was not observed. The low concentration of such species is probably the reason that the dissociation of CO and the Boudouard reaction are negligible [26].

### 3.5. Stability of the adsorbed CO species

Data on the stability of adsorbed CO species in different atmospheres are shown in Table 1. The presence of gas phase CO cannot be excluded in these TPR experiments, but the concentration should be lower than the sensitivity limit of the mass-spectrometer (0.03 vol.%). It is seen that the dicarbonyl Rh species is more stable than the linear adsorbed species. This is in accordance with the data of Dictor and Roberts [18] for the  $\text{Rh}/\text{Al}_2\text{O}_3$  catalyst treated for a short time in  $\text{O}_2$  at 673 K. An opposite order follows from the data of Trautman and Baerns [14] for the uncalcined Rh catalysts on different supports and from the data of Li and Gonzalez [21] for the  $\text{Rh}/\text{SiO}_2$  catalyst. Rh-support interaction does not take place in the latter catalyst [2] so that the dispersed Rh oxide species cannot be formed.

The stability of the dicarbonyl Rh species in He did not depend on the initial treatment prior to the CO interaction. The stability in a He flow was the same after the interaction of CO with (1) the catalyst oxidized at 823 K, (2) the catalyst reduced at 473 K by  $\text{H}_2$ . Oxygen and hydrogen do not interact with the dicarbonyl Rh species at 423 K. Interaction with  $\text{O}_2$  causes decomposition at a lower temperature than interaction with  $\text{H}_2$  (Table 1). Oxidation of isolated  $\text{Rh}^+$  species into  $\text{Rh}^{3+}$  species is easier than the reduction of  $\text{Rh}^+$  ions strongly interacting with an alumina support. The dicarbonyl species are relatively far apart because of the very low Rh content in the sample and high alumina surface area. Interaction of  $\text{Rh}^+$  with defect sites of alumina decreases its mobility and this hampers the reductive association of  $\text{Rh}^+$  ions producing metallic particles.

### 3.6. Interaction of CO and $\text{H}_2$ with either the reduced or the oxidized catalyst

Methane was formed in the reaction of CO with  $\text{H}_2$  on both the reduced and oxidized catalyst. In these experiments, the catalyst was reduced by  $\text{H}_2$  or oxidized by  $\text{O}_2$  at 823 K, and then after cooling in He it was heated in a  $\text{CO}/\text{H}_2$  mixture from 423 to 823 K. After reaching 823 K the spectra were taken and the gas phase composition was determined by the mass-spectrometer. The conversion of CO into  $\text{CH}_4$  amounted to 2.2% and did not change noticeably with time on the reduced catalyst. Only the very weak band of the linear species was observed. The conversion decreased with



time from 2.8 to 1.9% on the oxidized catalyst (Fig. 6). The dicarbonyl species was the main CO species on the catalyst in this case. The intensity of the dicarbonyl band also decreased with time (Fig. 6), thus reflecting the deactivation process.

The question rises whether or not the dicarbonyl species are important intermediates in the CO hydrogenation reaction. CO dissociation is a critical step in this reaction [35]. It is almost negligible on the flat Rh surfaces [35,36], but significantly proceeds on the surfaces containing defects [35]. CO dissociation on the metallic Rh should be faster than on  $\text{Rh}^+$  ions, because of back donation of electrons from the metal to adsorbed CO which weakens C–O bond and is responsible for CO dissociation [37]. Such back-bonding is practically absent with oxides [37]. Consequently the direct participation of the dicarbonyl species as an important intermediate in CO hydrogenation is not likely. Another reason for this is the stability of the dicarbonyl species which is higher than that of the linear CO

species in  $\text{H}_2$  (Table 1). In CO hydrogenation an apparent dependence of the rate of reaction on the bond energy of adsorbed CO is observed [38].

The deactivation of the catalyst can be explained in terms of the sintering of the Rh particles. It seems likely that when the dicarbonyl species are observed on the catalyst, i.e., when dispersed  $\text{Rh}^+$  ions are present, the other fraction, namely that of metallic Rh, is more dispersed than that produced by the reduction of the catalyst by  $\text{H}_2$ . The growth of the particles proceeds first through the formation of roughened two-dimensional particles, followed by the formation of three-dimensional particles. The bulk Rh atoms do not participate directly in the hydrogenation. The influence of the oxidation on the roughening of the Rh surface and on the catalytic activity has been proved in [35,39]. Hence, roughened Rh crystallites are more active in the hydrogenation than the crystallites after sintering in hydrogen.

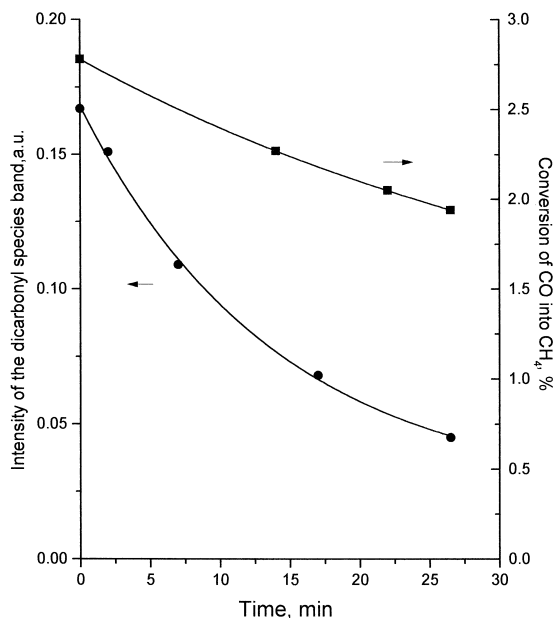


Fig. 6. Correlation between the intensity of the band of the dicarbonyl species at  $2017\text{ cm}^{-1}$  and the conversion of CO in methanation at 823 K on the oxidized catalyst. Composition of the feed—10.0 vol.% CO/13.5 vol.%  $\text{H}_2$ /76.5 vol.% He.

#### 4. Conclusions

The nature, stability and reactivity of CO adsorbed species on a 0.05 wt.%  $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$  catalyst were studied by DRIFTS. The present work shows again the power of FTIRS of adsorbed CO for the characterization of the state of Rh even in catalysts with a very low metal content. Other physical techniques are insufficiently sensitive for such a study.

Only the linear CO adsorbed species was observed on the catalyst reduced by  $\text{H}_2$  at 823 K. Its stability is lower and its reactivity with respect to  $\text{O}_2$ ,  $\text{H}_2$  and steam is higher than that of the dicarbonyl species. The very stable dicarbonyl species, associated with  $\text{Rh}^+$  ions, was obtained during the interaction of CO with the oxidized catalyst or with the catalyst reduced by  $\text{H}_2$  at 473–573 K. Rh sites in the sample are inhomogeneous. The dicarbonyl Rh species are partially removed by steam at 423 or 573 K,

while another fraction is removed only at higher temperatures. A fraction of Rh oxide is easily reduced into Rh metal, by CO at 423 K, while another fraction cannot be reduced completely by CO at temperatures up to 823 K. CO dissociation does not explain the difficulty of reducing the Rh completely into the metallic state. Disintegration and agglomeration of Rh particles under the joint action of CO and hydroxyl groups is not important for the catalyst studied. The initial methanation activity of the oxidized catalyst is higher than that of the reduced one. The concentration of the dicarbonyl species reflects the sintering processes of the metallic Rh particles. The higher the concentration of the dicarbonyl species, the more metallic Rh is dispersed.

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