CO scrambling with reactive oxygen species on vanadium promoted rhodium catalysts

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Well reduced silica-supported rhodium catalysts contain oxygen species that are able to participate in reactions. Adsorbed CO molecules were demonstrated to exchange their oxygen atoms with oxygen atoms from these catalysts. The amount of such reactive oxygen is increased by a vanadium promoter. Using infrared adsorption, the scrambling of $^{13}C^{18}O$ to $^{13}C^{16}O$ was studied as a function of the temperature. The vanadium promoter decreases the temperature for CO scrambling. Linear adsorbed CO is the preferred initial state for this process.

Keywords: CO scrambling; rhodium catalysts; vanadium promoter; IR

1. Introduction

Supported rhodium catalysts are of interest in synthesis gas reactions, due to their activity for the formation of C_{2+} oxygenates [1,2]. The formation of these products is related to the addition of less noble transition metal promoters [3–12]. The addition of a vanadium compound has been shown to increase both the activity and selectivity for the formation of ethanal and ethanol [13–18]. Although the direct formation of these products from synthesis gas is not of economical interest, due to the low activity of the catalyst, the role of the promoter is of great fundamental interest [19–22].

The first elementary step in the overall reaction mechanism to form ethanol and hydrocarbons is CO dissociation. CO dissociation on rhodium is a difficult step. It does not occur on flat single crystals but can be performed on supported catalysts above 300°C. Recently, we demonstrated that this step is promoted by a vanadium promoter [22]. CO dissociation has often been studied using the Boudouard reaction,

$$2CO(a) \rightarrow C(a) + O(a) + CO(a) \rightarrow C(a) + CO_2(g). \quad (1)$$

After dissociation of an adsorbed CO molecule, the resulting oxygen atom is removed as CO_2. This implies that every CO_2 molecule formed corresponds with one surface carbon atom from a dissociated CO molecule. However, the formation of CO_2 is not always a proof for CO dissociation as we will demonstrate in this paper. Even on well reduced rhodium catalysts there are oxygen containing species that can be involved in reactions and can therefore be responsible for CO_2 formation. This will be demonstrated by the adsorption of $^{12}C^{18}O$. Further, the exchange of oxygen is studied by in situ Fourier transform infrared spectroscopy of adsorbed $^{13}C^{18}O$. The role of the vanadium promoter on these processes will be analysed.

2. Experimental

Catalysts. A 3 wt% rhodium catalyst on Grace 332 type silica was prepared by incipient wetness impregnation with an aqueous solution of $RhCl_3$. Vanadium was added by post impregnation. Also catalysts on Aerosil 200 type silica were prepared. An extended description of the preparation and pretreatment of the catalysts as well as their characterization can be found in ref. [22].

CO adsorption. In a micro flow reactor system 300 mg of the catalyst was reduced in situ at 300–450°C before each experiment. Subsequently CO was adsorbed from a flow of 40 ml/min of 0.5% CO in helium. For the experiments with labeled CO, $C^{18}O$ of MSD isotopes was used (97.6% ^{18}O). The products formed were analysed on line with a quadrupole mass spectrometer.

Infrared spectroscopy. The catalysts were reduced at 450°C for 2 h while the cell was kept at 80°C to desorb water. The catalyst was cooled to 25°C where the reference spectrum was taken. $^{13}C^{18}O$ (MSD isotopes) was adsorbed at 10 mbar. The catalyst was heated to a special temperature, kept there for 5 min and subsequently cooled to 25°C where the adsorption spectra were measured. This process was repeated while increasing the heating temperature. The spectra were taken in transition mode at open vacuum.

3. Results

CO adsorption at elevated temperatures, on the reduced rhodium and rhodium/vanadium catalyst, resulted in the formation of CO_2 as shown in fig. 1.

Fig. 1 shows that the vanadium promoted catalyst forms the same amount of CO_2 approximately 100°C lower than on the rhodium catalyst. This could be in agreement with a previous conclusion that vanadium enhances CO dissociation [22], when assuming that CO is formed by the Boudouard reaction. It is of interest to look at all the products that are formed during the CO adsorption.

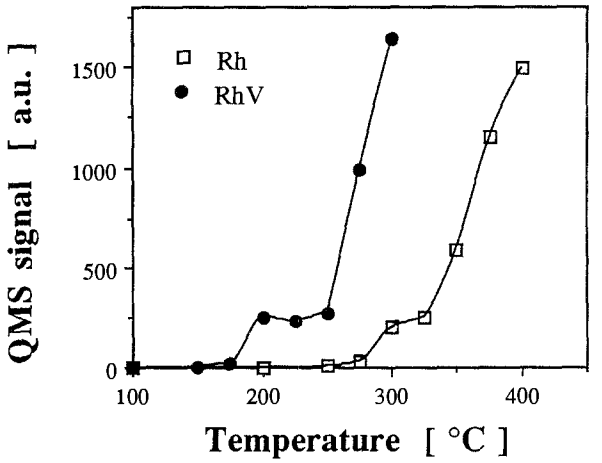

Fig. 1. The formation of CO_2 during CO adsorption at different temperatures on the rhodium and rhodium/vanadium catalyst on Aerosil 200.

The CO adsorption on the Rh and RhV catalyst is compared at the same CO_2 production levels, that is 400°C for the Rh catalyst and 300°C for the RhV catalyst. Fig. 2 shows all the products formed during CO adsorption at these temperatures.

When the CO/He flow is placed over a reduced catalyst, all the CO molecules adsorb for a special time. During that period some residual hydrogen desorbs, that was still adsorbed on the rhodium surface. When the catalyst surface is covered with CO, CO slips through the catalyst bed, but the signal does not return to its original level. At the same time hydrogen and CO_2 are produced.

To analyse if the CO_2 formed is due to the Boudouard reaction, the experiment was repeated using labeled $C^{18}O$. If CO_2 is only formed according to this reaction one would expect $C^{18}O_2$ as the only product. Both CO and CO_2 are analysed on their isotopic distribution.

Figs. 3a and 3b show that the first CO that desorbs from the catalyst is mainly $C^{16}O$! The $C^{18}O$ has exchanged its oxygen atom with a ^{16}O atom from the catalyst. The rate of this process decreases in time after the catalyst is fully covered with CO. However, after 500 s still about 15% of the CO molecules on the Rh catalyst is able to exchange its oxygen atom, and on the RhV catalyst about 30%.

The first CO_2 produced consisted mainly of $C^{16}O_2$ (see figs. 3c and 3d). After 500 s most of the CO_2 consists of $C^{16}O^{18}O$, which can be formed according to the water–gas-shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (2)$$

The fraction $C^{18}O_2$ formed is rather low, indicating that the Boudouard reaction is not the dominant reaction.

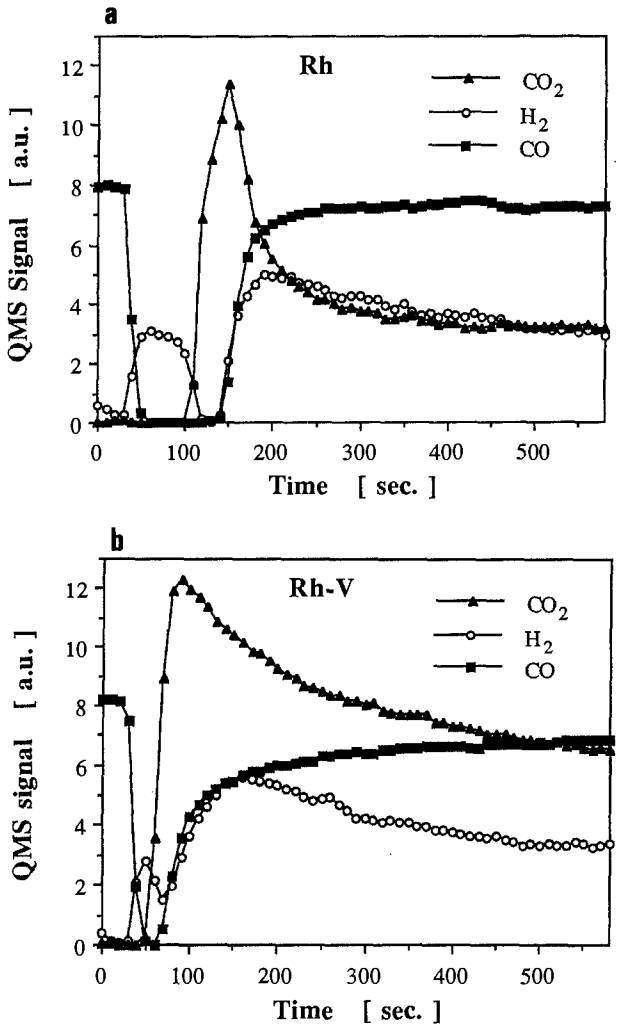

Fig. 2. Product formation upon CO adsorption in time on the Aerosil 200 supported catalysts. (a) Rh, CO adsorption at 400°C, (b) RhV, CO adsorption at 300°C.

The effect of adsorbed CO, scrambling its labeled oxygen atom with an unlabeled atom from the catalyst, has been studied using FT-IR. For this experiment $^{13}C^{18}O$ was used, which can form $^{13}C^{16}O$ after the exchange of an oxygen atom. These forms of CO have their IR absorption peaks at different wave number (fig. 4).

At low temperature both linear, bridge and twin adsorbed $^{13}C^{18}O$ are visible at the expected frequencies. An unexpected peak around 2015 cm^{-1} is observed on the rhodium–vanadium catalyst. Upon increasing the temperature an extra peak is appearing around 1980 cm^{-1} (indicated by the arrows). This peak is

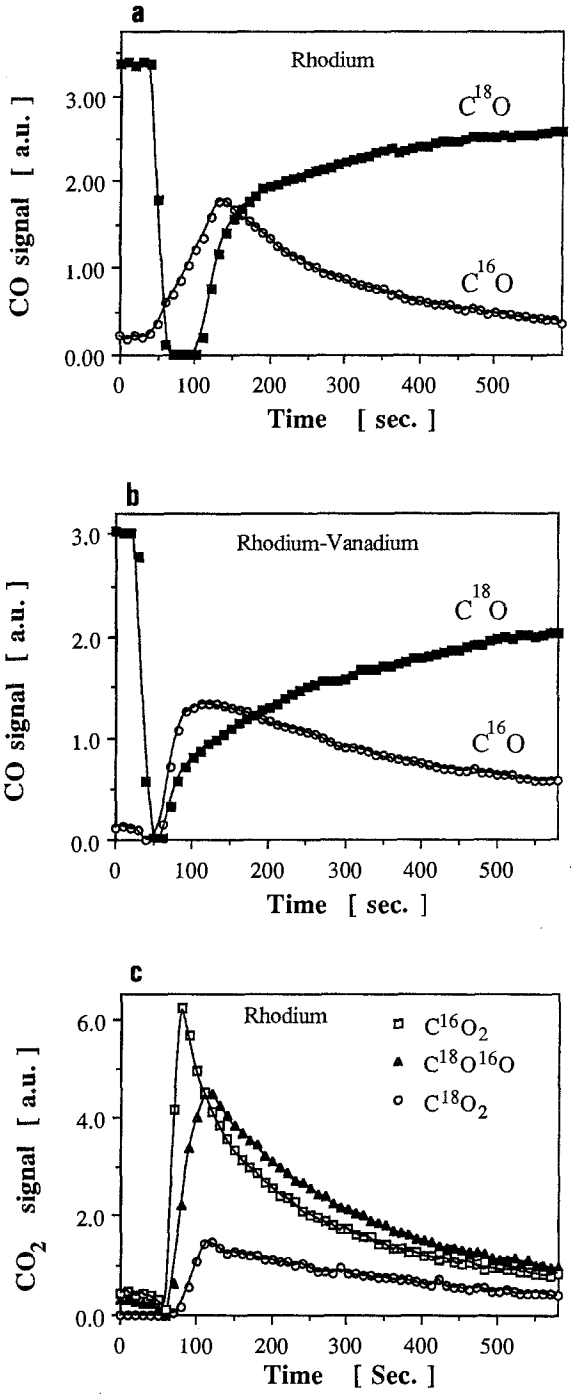

Fig. 3. Isotopic distribution of CO and CO_2 upon $C^{18}O$ adsorption on Rh at 400°C and RhV at 300°C.

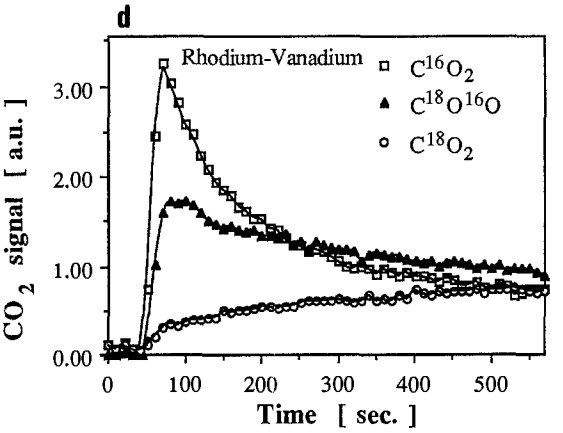

Fig. 3. Continued.

from linear adsorbed $^{13}C^{16}O$. On the rhodium catalyst also bridge adsorbed $^{13}C^{16}O$ is visible (at 300°C) that has exchanged its oxygen atom. On vanadium no oxygen exchanged bridge CO is observed.

The fraction of oxygen exchanged CO as a function of the temperature is shown in fig. 5.

The vanadium promoted catalyst lowers the temperature for the exchange of an oxygen atom with about 25°C on the Grace type silica catalysts.

4. Discussion

The CO_2 production during CO adsorption is always assisted with hydrogen production. This suggests that the CO_2 is rather formed according to the WGS reaction (2) than to the Boudouard reaction (1). This agrees with conclusions of Niwa and Lunsford [23] obtained on rhodium catalysts. We do not expect the water to be present in the reaction gases, because both the helium and hydrogen flow were purified by an additional Molecular Sieve column that was cooled at liquid nitrogen temperature. Therefore we think that the hydrogen is not formed from water molecules from the gas phase but more likely from hydroxyl groups remaining on the silica or adsorbed water on the silica.

The ratio of CO_2/H_2 formed during the CO adsorption is much higher on the vanadium promoted catalyst than on the rhodium catalyst. This indicates that CO_2 is not only formed by the water–gas-shift reaction or that the hydrogen desorbs slower from the vanadium promoted catalyst.

The adsorption experiments with labeled $C^{18}O$ also show that the Boudouard reaction is not mainly responsible for the CO_2 formed. Of interest is that a large fraction of the adsorbed CO molecules is able to exchange its oxygen atom. Apparently the well reduced catalysts contain still oxygen species that are able

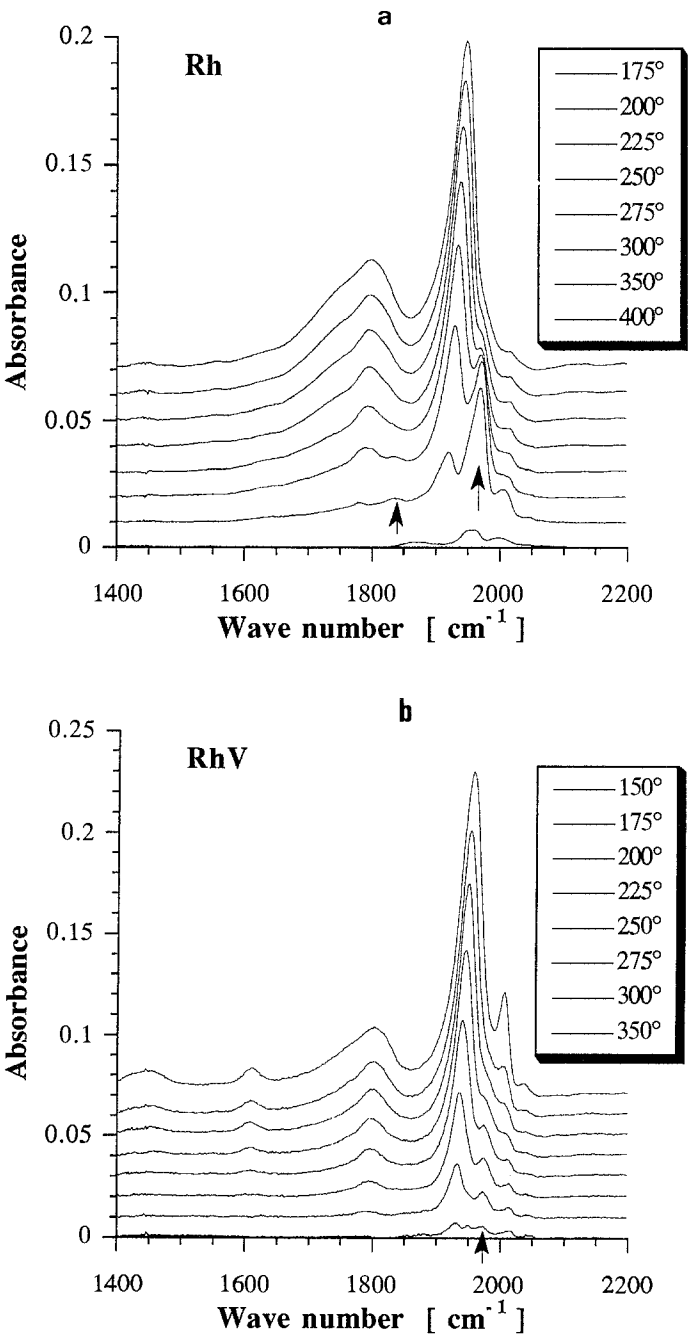

Fig. 4. FT-IR spectra of adsorbed $^{13}C^{18}O$ at different temperatures on the Grace supported catalysts. (a) Rh, (b) RhV.

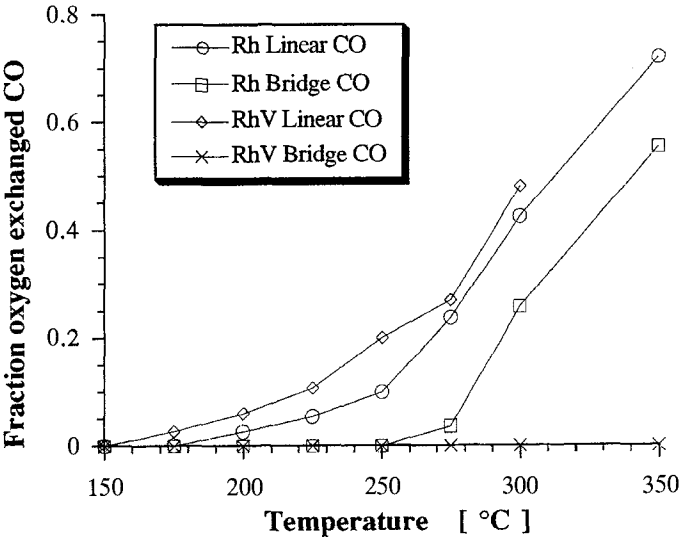

Fig. 5. Fraction of the linear and bridge adsorbed CO molecules that have exchanged an ^{18}O oxygen atom with an ^{16}O of the catalyst.

to participate in reactions at elevated temperatures. The reaction of $C^{18}O$ from the gas phase and ^{16}O species from the catalyst, does not result in the initial formation of $C^{18}O^{16}O$ but mainly in $C^{16}O_2$. This is due to a multiple scrambling of the CO_2 molecules. The dissociative readsorption of CO_2 at the temperatures applied is fast. Therefore, the ratio of $^{16}O/^{18}O$ in the CO_2 molecules is reflecting for this ration in the surface oxygen species. This ration is shifting in time from initially only ^{16}O to more and more ^{18}O (see fig. 3).

The importance of the presence of such oxygen species for catalysis has been previously observed by Orita et al. [24] on silica supported rhodium catalysts. These authors showed that oxygen atoms located on the silica can play an important role in the formation of oxygenated products like ethanal from synthesis gas. They performed a reaction with $C^{18}O/H_2$ over Rh/SiO_2 and demonstrated that the oxygen atom in the ethanal molecules formed consisted for 50% of ^{16}O and for 50% of ^{18}O.

The process of adsorbed CO scrambling its oxygen atom, can be nicely studied with IR spectroscopy. When $^{13}C^{18}O$ was observed, $^{13}C^{16}O$ appeared with an increase of temperature. Vanadium lowers the temperature for this scrambling with about 25°C on the Grace supported catalysts. This is much less than the temperature difference of 100°C for CO_2 formation on the Aerosil supported catalysts. This may be due to the presence of some small amounts of potassium (200 ppm) and iron (440 ppm) on the Grace supported catalysts which can induce some promotion effects [25,26].

Interesting is that the CO scrambling can be individually followed on the linear and bridge adsorbed CO adsorption sites. On the rhodium catalyst the

CO exchange occurs preferentially on the linear sites, while on the vanadium catalyst the exchange occurs only at this site. This is unexpected because CO is better activated on the bridge adsorption site, which has been indicated as the favourite position for CO dissociation [27].

For the CO scrambling one can propose three mechanisms. First: an adsorbed CO molecule dissociates and subsequently the resulting surface carbon recombines with an oxygen atom from the catalyst to form CO again. Second: a CO_2 like intermediate is formed, from CO and an oxygen atom from the catalyst, that subsequently dissociates on the rhodium surface to form CO with another oxygen atom. Third: a four-center CO $\cdots$ CO complex can act as reaction intermediate as proposed by Yamada et Tamaru [28]. In this case $Rh^I(CO)_2$ species [29,30] are possibly involved. Our results give some support for the second mechanism. As already indicated, the favourite site for CO dissociation is not the preferred site for CO scrambling, which does not fit with mechanism (1). Further the CO scrambling is assisted with the formation of CO_2, indicating that CO_2 may be a reaction intermediate. At elevated temperature the CO on the gem dicarbonyl species desorb before exchanging an oxygen atom. This agrees partly with the conclusions of Panayotov et al. [31]. They concluded that CO scrambling occurs via a non-dissociative mechanism on Rh^0 sites. However, they proposed a direct interaction between two adsorbed CO molecules. They did not have evidence for the reactive oxygen species as reported here.

From fig. 5 one can also draw conclusions in terms of the mobility of CO to move from a linear site to a bridge site. This mobility does not exist at any temperature on the rhodium–vanadium catalyst, because no $C^{16}O$ is visible on bridge sites while it is present on linear sites. Also, on the rhodium catalysts there does not exist a fully dynamic equilibrium between linear and bridge adsorbed CO. It is not clear whether the $C^{16}O$ molecules on bridge sites are formed on these sites or that they have migrated from linear to bridge sites.

5. Conclusions

After reduction at 450°C, silica supported rhodium catalysts still contain oxygen species that are able to participate in reactions. Both the amount as well as the reactivity of these oxygen species are increased by a vanadium promoter. These oxygen atoms are most likely located on the silica support in the form of hydroxyl groups. These species can be used to oxidise CO to CO_2, which is assisted with the formation of hydrogen. Therefore the formation of CO_2 is not a full prove for CO dissociation by the Boudouard reaction. Oxygen species can also exchange with the oxygen atom of an adsorbed CO molecule. This process occurs preferentially on linear CO adsorption sites. The exchange between CO on linear sites with CO on bridge sites is slow.

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