In situ FTIR spectroscopy on rhodium-exchanged NaX zeolite with different metal dispersion during syngas reaction

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In situ FTIR spectroscopy has been applied to study the reason of the different selectivity behaviour of rhodium in the CO hydrogenation reaction in dependence on the different particle size. Several forms of molecularly adsorbed CO are observed, such as linearly- and bridged-bonded CO on metallic rhodium as well as dicarbonyl species with Rh(I) centres formed by oxidation of Rh(0) with protons in presence of CO. Furthermore, non-reactive formate, acetate, and carbonate species are produced as side products of the reaction. The higher selectivity to oxygenates, particularly to methanol, is explained by the existence of multiple-bonded CO present only on small rhodium crystallites. The multiple-bonded CO formed at low temperatures is converted at higher temperatures to the highly reactive formyl species, which is hydrogenated to methanol.

Keywords: faujasite-hosted rhodium; in situ FTIR spectroscopy; CO hydrogenation; rhodium dispersion; methanol selectivity

1. Introduction

The influence of the metal dispersion of supported noble metal catalysts on the activity and the selectivity in synthesis gas reactions has been studied intensively, but the results are still controversial. The syngas reaction on noble metals has been described to be a structure sensitive reaction, mostly, with an antipathetic structure sensitivity [1]. Arakawa et al. [2] have found for rhodium on silica a decrease of the activity with increasing dispersion. Kellner et al. [3] have observed a dramatic decrease of the activity for ruthenium on alumina when the dispersion becomes larger than 0.7. The question how the selectivity to hydrocarbons and to oxygenates

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depends on the metal particle size is of particular interest. In the case of palladium catalysts the situation is much more complicated. So, Poutsma et al. [4] and Ichikawa et al. [5] have reported on a high selectivity to methanol on large palladium particles supported on silica, whereas Hahm et al. [6] have observed an increase of the selectivity to methanol with increasing dispersion of palladium on silica. Similar results are described by Fajula et al. [7] for palladium supported on different carriers. Recently, Cavalcanti et al. [8] have reported on a higher selectivity to methanol on larger palladium crystallites dispersed in NaY compared with smaller ones. Jaeger et al. [9] have found a higher selectivity to methanol on small particles of platinum or palladium dispersed on NaX compared with larger crystallites of the corresponding elements. The same result has been obtained by using different rhodium dispersions on NaX [10]. Selectivity was expressed as a ratio of turnover numbers ($S = \mathrm{TOF(methanol)}/\mathrm{TOF(methane)}$) and a relative selectivity as a ratio of selectivities ($S_{\mathrm{rel}} = S(\text{fine metal dispersion})/S(\text{coarse metal dispersion})$). For surface average diameters of Rh particles of 1.3 and 4.6 nm, respectively, a relative selectivity $S_{\mathrm{rel}} = 2.7$ has been reported in ref. [10]. On highly dispersed rhodium a high selectivity to methanol has been also observed in several studies [11–14]. An improved oxygenate selectivity would be achieved by a suitable CO activation or by stabilization of oxygenated intermediates [15].

In order to obtain more detailed information, in situ FTIR experiments in flowing syngas in the temperature range of 300–570 K have been performed, since FTIR spectroscopy has proved to be a powerful method for the study of intermediates in syngas reaction [16–25].

2. Experimental

2.1. CATALYST PREPARATION

The precursor was prepared by ion exchange of NaX (Si/Al ratio of 1.2) with $[Rh(NH_3)_5Cl]Cl_2$ as described in ref. [10]. The formation of small particles was ensured by calcination in oxygen followed by reduction with hydrogen (sample RhCl/O). Decomposition of the rhodium complex in an inert gas atmosphere, for instance in nitrogen, results in the formation of larger metal particles (RhCl/N). Both the formation of small and large rhodium particles located in the NaX matrix was carried out in situ in the IR cell.

2.2. IN SITU IR SPECTROSCOPY

For IR spectroscopic experiments self supporting disks of the samples with a "weight" of ca. 9 mg/cm^2 were mounted in a high pressure cell equipped with CaF_2 windows. The spectra were recorded with an FTIR spectrometer IRF 180 at a resolution of 2 cm^{-1}. The pretreatment conditions were the following:

(1) The dried precursor was heated in flowing oxygen (100 ml/min) to 623 K (2 K/min) and held for 3 h, then purged with nitrogen at r.t., switched to a hydrogen stream (30 ml/min) and heated to 573 K (4 K/min) and held for 2 h. Finally, hydrogen was replaced by nitrogen (30 ml/min) to remove adsorbed hydrogen. In order to follow the decomposition transmission spectra were recorded at several temperatures during the heating as well as cooling process.

(2) The dried precursor was heated in flowing nitrogen (30 ml/min) to 623 K (2 K/min) and held for 2 h. Again spectra during heating and cooling periods were recorded.

After the different pretreatments ensuring the formation of small and large rhodium particles the as-pretreated wafers were exposed to a carbon monoxide/hydrogen mixture (1 : 2) at a pressure of 0.2 MPa and a flow rate of 20 ml/min. Spectra were recorded at different temperatures in the range of 300–570 K in transmittance; they were taken for the time being 30 min after the desired temperature was reached and after 5 h at 570 K, respectively. The spectra are presented as absorbance after subtracting the background absorption of the samples measured at the corresponding temperatures in a flow of nitrogen after the pretreatment had been performed. This procedure is important to avoid the influence of a different background of the solid sample in the case of measuring at different temperatures. Furthermore, the spectra were baseline corrected using the software of spectra calc for estimation of the band intensities in terms of the integrated area.

2.3. TPR MEASUREMENTS AND HYDROGEN CHEMISORPTION

The temperature-programmed reduction was carried out in a flow apparatus, using a 5% hydrogen in argon mixture at a gas flow rate of ca. 20 ml/min and a catharometric detector as described by Lieske et al. [26]. After pretreatment at 523 K for 3 h, either in oxygen to obtain small particles or argon to obtain large particles, the hydrogen consumption was measured at a heating rate of 3.5 K/min between r.t. and 673 K for the determination of the reduction degree. Then the sample was cooled to r.t. and the consumed amount of hydrogen was determined as the chemisorbed hydrogen on metallic rhodium. Heating again with a rate of 20 K/s up to 673 K gives the amount of desorbed hydrogen. Using these data the metal dispersion was calculated as described by Benesi et al. [27].

3. Results and discussion

3.1. TPR AND HYDROGEN CHEMISORPTION

The results of temperature-programmed reduction show the complete reduction of the oxygen treated sample by hydrogen at 573 K and no further reduction of the sample, which was heated in the inert gas atmosphere (table 1). This means

Table 1
Hydrogen consumption during temperature programmed reduction and amount of hydrogen adsorbed and desorbed, respectively, on Rh supported on NaX-zeolite (RhCl/N) – pretreated in nitrogen or argon, RhCl/O – pretreated in oxygen; Rh content 5.7 wt% [10]; theoretical H_2 consumption: 831 μmol/g)

	RhCl/N	RhCl/O
H_2 (μmol H_2/g)		
TPR-consumption	0	882
adsorption	52	129
desorption	46	135
dispersion (H/Rh)	0.18	0.48
S	80	214
crystallite size d (nm) [a]		
estimated from dispersion	5.0	1.9
estimated from TEM [10]	4.6	1.3
selectivity ratio (TOF(methanol)/TOF(methane))	4.0×10^{-2}	10.7×10^{-2}

[a] d (nm) $= 5 \times 1000/\rho S$, ρ = density of the metal, S = surface area in m^2/g_{Rh} calculated from H/Rh, S(small part.)/S(large part.) = 2.7.

for the oxygen-treated samples that Rh(III) is reduced by hydrogen to Rh(0), whereas the pretreatment in an inert gas atmosphere results in an autoreduction by ammonia and in the formation of metallic rhodium already before hydrogen treatment.

Furthermore, it is evident that the hydrogen adsorption capacity of RhCl/O is distinctly higher than that of RhCl/N. The dispersion of rhodium is more than twice higher for RhCl/O. The surface average diameter of the metal particles has been estimated by the equation given in table 1 using a model with cubic metal particles. The values are in good agreement with the ones found in ref. [10] by transmission electron microscopy.

3.2. INFRARED SPECTROSCOPY

Fig. 1 shows the spectra of the ion exchanged sample during heating in nitrogen at the indicated temperatures. The intensity of the broad band at 1338 cm^{-1} assigned to ammonia decreases with increasing temperature accompanied by a shift to 1314 cm^{-1} indicating the decomposition of the ammine complex. This process is finished at 570 K as demonstrated by the disappearance of the absorption band.

The spectra taken during calcination in oxygen and subsequent reduction with hydrogen are more complex as shown in figs. 2a and 2b. The maximum of the broad absorption band is shifted from 1330 cm^{-1} (spectrum a) to 1380 cm^{-1} (spectrum d of fig. 2a) when the calcination temperature has been increased. The exis-

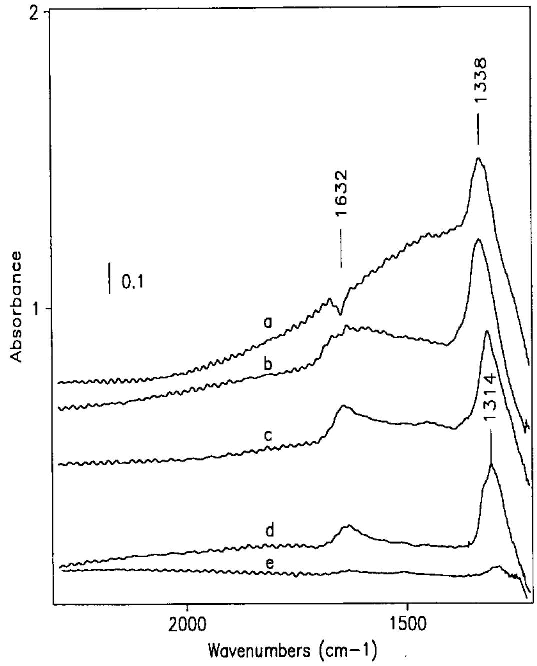

Fig. 1. Infrared spectra of NaX zeolite exchanged with $[Rh(NH_3)_5Cl]Cl_2$ treated in flowing nitrogen at 300 K (a), 400 K (b), 470 K (c), 520 K (d), and 570 K (e).

tence of this band assigned to ammonia coordinated to Rh even after calcination at 573 K points to a significant stability of rhodium(III) ammine complexes in oxygen. Only reduction with hydrogen results in the disappearance of all bands (spectrum d of fig. 2b). During this reduction a small band at 1450 cm^{-1} appears (see spectrum b of fig. 2b), which can be assigned to NH_4^+ [28] probably bonded to the zeolite lattice. Furthermore, the band at 1643 cm^{-1} has to be ascribed to adsorbed water formed during the reduction process.

Fig. 3 shows spectra obtained by interaction of syngas with RhCl/N at different temperatures. Immediately, small bands appear at r.t. only in the CO stretching vibration region centred at 2100 and near 2010 cm^{-1}. At 470 K additional bands at 1850, 1580, 1465, 1430, and a shoulder at 1396 cm^{-1} are developed. Furthermore, two very small bands at 1710 and 1640 cm^{-1} can be obtained (spectrum b). At 570 K these latter bands are absent and very small bands or shoulders appear at 1350, 1624, and 1663 cm^{-1} (spectrum d).

The corresponding spectra for the sample RhCl/O (fig. 4) show more intense bands in the region of the molecularly adsorbed CO. Besides the bands at 2100 and near 2010 cm^{-1}, a broad absorption centred at 1786, an intense band at 1645, and a very small band at 1580 cm^{-1} are observed already at r.t. (spectrum a). At 470 K the intensity of the bands at 2100, 2010, and 1580 cm^{-1} increases, the maximum of the broad absorption is shifted to 1768 cm^{-1}, which contains now a distinct shoulder near 1855 cm^{-1}, and new bands appear at 1471 and 1398 cm^{-1}. With

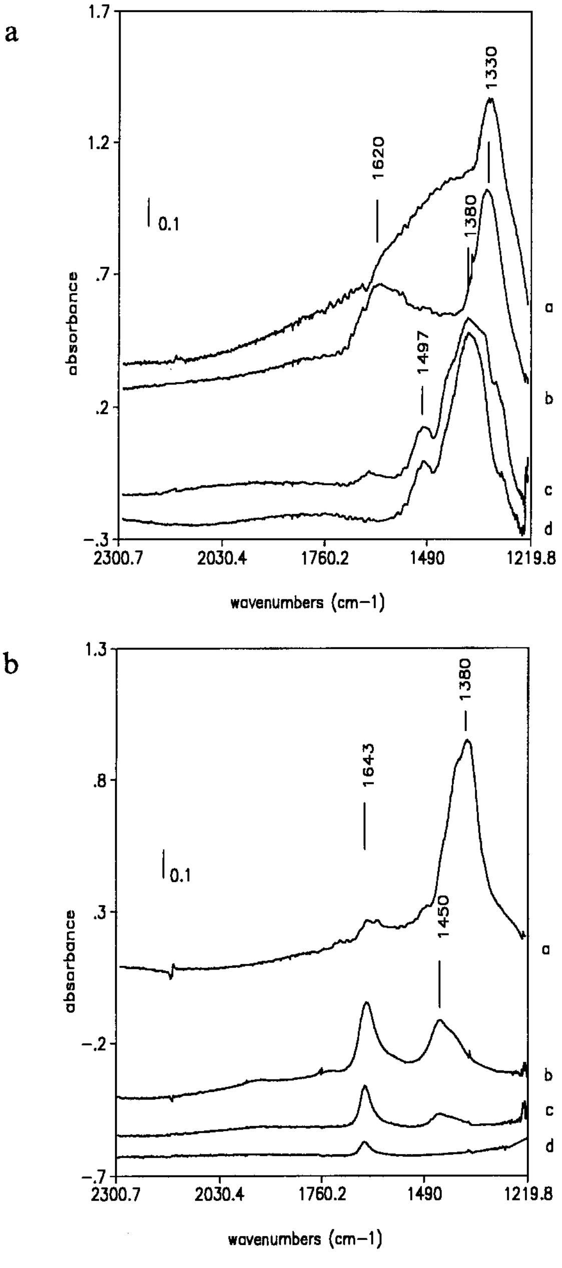

Fig. 2. (a) Infrared spectra of NaX zeolite exchanged with $[Rh(NH_3)_5Cl]Cl_2$ treated in flowing oxygen at 300 K (a), 400 K (b), 520 K (c), and 570 K (d). (b) Infrared spectra of the oxygen calcined sample treated in flowing hydrogen at 300 K (a), 470 K (b), 520 K (c), and 570 K (d).

further increase of the reaction temperature all bands of molecularly adsorbed CO and the band at 1398 cm^{-1} decrease in intensity, whereas the intensities of the bands at 1580 and 1465 cm^{-1} rapidly grow. Moreover, a new band at 1430 cm^{-1} developed at 520 K becomes very intense at 570 K. Furthermore, it should be

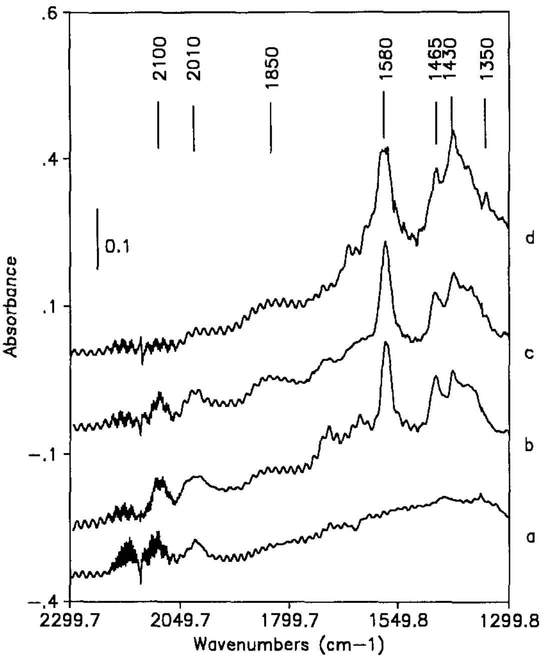

Fig. 3. Infrared spectra of RhCl/N under flowing synthesis gas at 300 K (a), 470 K (b), 520 K (c), and 570 K (d).

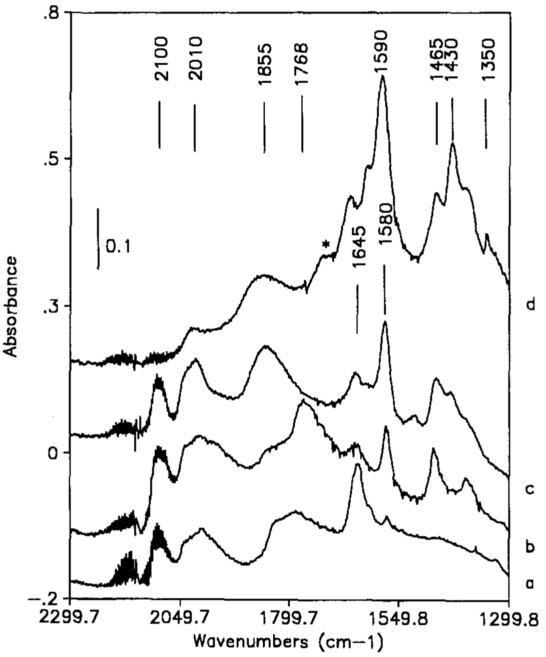

Fig. 4. Infrared spectra of RhCl/O under flowing synthesis gas at 300 K (a), 470 K (b), 520 K (c), and 570 K (d).

noted that the band at 1768 cm^{-1} (spectrum b) disappears and simultaneously the band at 1855 cm^{-1} is developed, when the temperature rises to 520 K (spectrum c). Finally, a small shoulder at 1720 cm^{-1} (indicated by the asterisk in spectrum d), a shift of the band at 1580 to 1590 cm^{-1}, and small bands at 1661, 1624, 1350, and 1400 cm^{-1} can be observed at 570 K. The assignment of the IR bands, considering the results of the known literature, has been summarized in table 2.

After 5 h time-on-stream at 570 K the catalyst waver was cooled to r.t. in flowing syngas, the latter was replaced by nitrogen and then the temperature was increased to 570 K. In fig. 5 the spectra are shown for both catalysts at r.t. (a and b, respectively) and at 570 K (c and d, respectively) in the nitrogen stream. After thermal treatment in nitrogen the sample was again cooled to r.t. and nitrogen was now replaced by hydrogen. The spectra e and f of fig. 5 show the result of the hydrogen treatment at 570 K. These additional experiments indicate that the bands for formate, acetate, and carbonate species do not disappear neither by thermal treatment up to 570 K (spectra c and d) nor by treatment with hydrogen at 570 K (spectra e and f). The molecular adsorbed CO, however, (absorption bands in the region 2100–1800 cm^{-1}) is desorbed partly already at r.t. and completely by thermal treatment in the nitrogen stream.

For comparison of both catalysts the main spectroscopic results are summarized in table 2. In presence of syngas carbon monoxide is molecularly adsorbed at temperatures up to 520 K in at least three different forms, namely as linearly- and bridged-bonded CO on metallic rhodium and in the form of the gem-dicarbonyl structure $Rh(I)(CO)_2$. The latter is absent at 570 K. The occurrence of the gem-dicarbonyl can be explained either by incomplete reduction of the precursor or by oxidation of metallic rhodium in presence of carbon monoxide and water or hydroxyl groups of the support [29]. We prefer the latter explanation because complete reduction follows from the TPR results. Besides the differences of the band intensities, which will be discussed later, the main difference for both catalysts should be the

Table 2
Wavenumbers of the absorption bands and their assignment to adsorbed surface species [a]

RhCl/O	RhCl/N	Assignment
2100	2100	$Rh(I)(CO)_2$ [30]
2010 vbr	2010 vbr	$Rh(I)(CO)_2$, Rh(0)CO [30]
1855 vbr	1850 vbr	$Rh_2(0)CO$ [30]
1768–1786 vbr	–	$Rh_3(0)CO$ [2]
1580–1590	1580	formate, acetate [22,37,38]
1465–1471	1465	acetate [37,38]
1430	1430	carbonate? [17]
1398–1400	1396	formate [22]
1350	1350	formate [22,37]
1645–1661	1640–1663	acetyl [2]
1720	–	formyl [38]

[a] vbr=very broad.

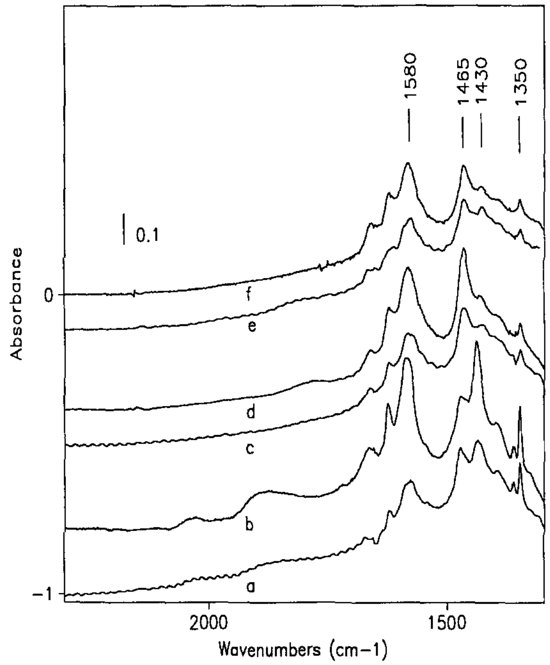

Fig. 5. Infrared spectra of the samples RhCl/N and RhCl/O after 5 h time-on-stream at 570 K in syngas and subsequent cooling to 300 K (see text); RhCl/N at 300 K in nitrogen (a), RhCl/O at 300 K in nitrogen (b), RhCl/N at 570 K in nitrogen (c), RhCl/O at 570 K in nitrogen (d), RhCl/N at 570 K in hydrogen (e), RhCl/O at 570 K in hydrogen (f).

position of the band for bridged-bonded CO. In general, an absorption in the spectral region 2000–1650 cm^{-1} is ascribed to bridged-bonded carbon monoxide on metals [30]. On Rh the band of bridged-bonded CO is usually observed in the region of 2000–1800 cm^{-1}. There are some possibilities to explain the unusually low frequency position of the band in the range 1786–1768 cm^{-1} for the RhCl/O sample:

– formation of multiple-bonded CO on highly dispersed Rh [2] including the possibility of the formation of Rh complexes, for instance $Rh_6(CO)_{16}$ [31,32];

– formation of the so-called tilted structure with carbon bound to rhodium and oxygen coordinated to Al^{3+} [33];

– clustering of CO around the Na forming a band with a lower vibration frequency. A band at 1795 cm^{-1} has been described by Angevaare et al. [34] for potassium promoted Rh on SiO_2.

Considering the high intensity of this band observed in our experiments, the assignment to the tilted structure seems to be unlikely, but from our results it is difficult to distinguish between the possible influence of sodium ions on the band position or the formation of multiple-bonded CO. The influence of Na^+ on the adsorption properties of rhodium should be the same for small as well as for large metal particles, although a more effective influence of sodium on the small particles cannot be excluded definitively. Nevertheless, the most possible explanation of the low frequency band should be the multiple-bonded CO formed only on small rhodium crystallites and absent on larger ones. The reason for the formation of this structure only on small particles may be the lower coordination number for surface metal atoms.

In order to compare the intensities of the bands for the molecularly adsorbed CO on both catalysts an attempt has been made to estimate the intensities for the different bands. There are, however, difficulties to separate the bands for linearly-bonded CO and the low frequency band of the dicarbonyl structure. On the other hand it is clearly seen from the band shape that the broad absorption near 2010 cm^{-1} consists of more than one band. Besides the bands of $Rh(I)(CO)_2$ and Rh(0)(CO) the formation of rhodium carbonyl hydrides should be very likely at the reaction conditions used in this study. Solymosi et al. [35] have assigned bands at 2048 and 2030 cm^{-1} to Rh carbonyl hydrides.

Assuming that the intensity of both bands of the twin structure is the same, the intensity for the linear band has been calculated and included in table 3 as the intensity of the band assigned to the linearly-bonded CO. The same intensity for both bands of the gem-dicarbonyl has been reported by Yamanais et al. [36] for carbon monoxide adsorbed on NaX exchanged with $RhCl_3$. The results of our rough estimation show a similar intensity ratio (I for RhCl/O to I for RhCl/N) of the bands at 2100, 2010 and 1855 cm^{-1} as it has been found for the ratio of the surface area of both catalysts by hydrogen chemisorption (see table 1). But this is not true if the low frequency band of the multiple-bonded CO is included, which is only present on the small rhodium particles up to 470 K. The intensity ratio of the bridged-bonded CO, measured at temperatures up to 470 K, is distinctly higher as it should be expected from the surface area of rhodium (see table 3).

From these results the following conclusions about the catalytic properties can be drawn: The higher selectivity to oxygenates particularly to methanol on small rhodium crystallites (see table 1) can be explained by the existence of multiple-

Table 3
Intensity of the IR bands of adsorbed CO measured at different temperatures and intensity ratio for small and large rhodium particles on Rh supported on NaX-zeolite

Reaction temp. (K)	Intensity							Intensity ratio		
	small particles (RhCl/O)				large particles (RhCl/N)			I(small part.)/I(large part.)		
	2100	2010	1855	1768	2100	2010	1850	2100	2010	1855
470	3.79	3.04	–	9.76	1.77	0.64	1.19	2.1	4.8	8.2[a]
520	2.32	2.76	8.48	–	0.94	1.22	2.33	2.5	3.1	3.6
570	–	1.08	4.83	–	–	0.87	1.24	–	1.2	3.2

[a] This value is estimated from the intensity of the band at 1768 cm^{-1} and the intensity of the band at 1850 cm^{-1} (see text). The intensity for the linear band has been calculated by subtraction of the area of the band at 2100 cm^{-1} from the area of the broad absorption near 2010 cm^{-1}.

bonded CO as a precursor for intermediate formyl species. At low temperatures the multiple-bonded CO is formed which is converted at higher temperatures to the highly reactive formyl species. This species is very fast hydrogenated to methanol and, therefore, the surface concentration may be low and its detection by infrared spectroscopy could be difficult. Furthermore, formate and acetate species are formed via formyl and acetyl species, respectively. The formate and acetate surface compounds are very stable at thermal treatment as well as at treatment with pure hydrogen. This result is in good agreement with investigations of other authors [2,37] and shows that formate and acetate are not intermediates for the formation of alcohols but they may be side products, which decrease the overall catalytic activity with time-on-stream [10].

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