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Solid-state ion exchange of rhodium chloride with highly dealuminated Y-type zeolite DAY by thermal treatment and in the presence of carbon monoxide

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The solid-state ion exchange of Rh chloride with highly dealuminated Y zeolite has been studied by in situ FTIR spectroscopy. Thermal treatment in vacuum and calcination in oxygen up to 600°C results in an exchange limited to ca. 25% at temperatures higher than 400°C. The ion exchange can be performed much more effectively (over 50%) and at lower temperatures (100–150°C) in the presence of CO in the gas phase. A linear correlation has been found between the formation of well-defined $Rh(CO)_2^+$ species and the simultaneous loss of acid hydroxyl groups for samples treated at different conditions. From these results a model is proposed with the formation of Rh subcarbonyls, the migration of these species to the cation positions of the zeolite and, finally, the formation of the stable well-defined $Rh(CO)_2^+$ species at these positions as essential steps of the ion exchange in the presence of CO.

Keywords: Solid-state; ion exchange; dealuminated Y zeolite; rhodium catalysts; infrared spectroscopy; Rh dicarbonyl; acid hydroxyls

1. Introduction

Several methods have been applied to exchange transition metals into cationic positions of zeolites. Besides the conventional methods, such as the exchange with dilute aqueous solution or the incipient wetness impregnation, the solid-state reaction of a zeolite with metal salts or metal oxides has been used [1–4]. A complete exchange could be obtained only in some cases and under certain conditions [3]. The first noble metal exchanged zeolite has been prepared by Karge et al. [4] from a mixture of $PdCl_2$ and H-ZSM-5 by thermal treatment at 400°C in vacuum. The extent of exchange was followed using the change of the intensity of the infrared bands attributed to the acid bridging OH groups. The resulting product showed a consumption of 55% of the acid OH groups. In high silica zeolites the distance between the Al atoms in the framework is large and, therefore, the exchange is lim-

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ited by the geometric constraints of balancing fairly distant lattice charges by a polyvalent cation. The mechanism and the extent of solid-state exchange of these zeolites with low Al content is still under discussion [5]. The aim of the present work is, in this connection, the study of the solid-state ion exchange of rhodium into a highly dealuminated zeolite Y.

For the characterization of dispersed rhodium, the interaction of the samples with CO has been followed by IR spectroscopy. The interaction of CO with dispersed rhodium supported on high-surface oxides results in the formation of linearly ($\nu_{(CO)} = 2080-2000$ cm^{-1}) and bridge-bonded CO ($\nu_{(CO)} = 2000-1750$ cm^{-1}) on metallic Rh and of dicarbonyl surface species with two CO molecules bound to one Rh atom, probably in the Rh^+ cationic form (band doublet with $\nu_{(CO)}$ at ca. 2100 and 2030 cm^{-1}) [6–12]. The band width of the corresponding carbonyl stretching modes is usually larger than 15 cm^{-1} and the actual position of the IR bands and their relative intensities depend on the support, the dispersion of Rh and the preparation and pretreatment method used.

On the other hand, dealuminated Y zeolite has been found as a unique material to form carbonyl and nitrosyl complexes on the surface with IR absorption bands much narrower and at wavenumbers and with intensity ratios independent of the preparation method or the sample pretreatment [13–16]. Such species should be regarded as well-defined complexes on the surface with the support acting as a kind of matrix and/or as a ligand. The surface sites of the support should have uniform structural and electronic properties in these cases, and it has been proposed that the complexes are localized at the isolated acid sites at the remaining Al-atoms in the zeolite framework [13,14,17]. The formation of those species should be regarded, therefore, as the result of an ion exchange.

2. Experimental

The DAY supplied by DEGUSSA has a Si/Al ratio of ca. 300. In order to obtain well powdered and mixed mechanical mixtures $RhCl_3$ and DAY were ground in an agate mortar. Two different ways were applied to perform the solid-state reaction.

(1) For solid-state exchange in vacuum the mixture containing 3 wt% $RhCl_3$ was pressed into self-supporting wafers, mounted in a cell of fused silica and connected to a vacuum and gas dosing line. The wafer was heated in situ (vacuum of ca. 10^{-3} Torr) to the required temperature, which was held for 30 min. The spectra were taken after cooling down the samples to room temperature (r.t.).

(2) For solid-state exchange in oxygen the powdered mixtures were heated ex situ in flowing O_2 to 400, 500, and 600°C, respectively, held for 5 h at that temperatures and cooled to r.t. The degree of exchange was determined by the decrease of the intensities of the bands assigned to the bridging OH groups.

The infrared spectra were measured with an FTIR spectrometer FTS 60-A

(BIORAD) at a resolution of 2 cm^{-1}. 256 scans were accumulated to obtain a good signal to noise ratio. The powdered samples were pressed into self-supporting wafers with a "weight" of 6–12 mg/cm^2 and mounted in the infrared cell as described above. The interaction with CO was studied by addition of 12 Torr of CO first at r.t., then at 100°C for 15 min, and finally at 150°C for 15 min. All spectra were measured at r.t. They are presented as absorbance after subtracting the background absorption of the samples and after subtracting the contribution of gaseous CO. In accordance to ref. [18] the spectra are normalized for the sample thickness by comparing the intensities of the absorption bands for the lattice vibration of the zeolite at 1870 and 2000 cm^{-1}. The intensities of the bands in the CO stretching vibration region were determined after band separation using the curve-fit program of Spectra Calc.

3. Results and discussion

3.1. SOLID-STATE EXCHANGE IN VACUUM

To follow the solid-state ion exchange the intensity of the absorption bands at 3631 (HF-band) and 3568 cm^{-1} (LF-band) was used as a measure of the extent of the ion exchange. The intensities of both bands decrease at temperatures above 400°C. Decreases in intensity of the HF band were 0, 15, 22 and 29% after treatments at 400°C (0.5 h), 500°C (0.5 h), 580°C (0.5 h) and 580°C (1 h), respectively. Corresponding decreases for the LF band were 0, 8, 11 and 22%.

CO adsorption has been used for further characterization of the product. Interaction with CO at r.t. results in the appearance of a broad absorption between 2100 and 2000 cm^{-1} (fig. 1a). This band can be assigned to linearly bonded CO and the band near 1890 cm^{-1} has to be assigned to bridged bonded CO on metallic Rh. Increasing this temperature to 150°C results in the growing of two narrow bands at 2118 and 2053 cm^{-1} (spectra b and c), assigned to a well-defined $Rh(CO)_2^+$ structure [13]. Furthermore, two bands at 2100 and 2035 cm^{-1} appear, the assignment of which will be discussed later. The spectra shown in fig. 1 clearly demonstrate that a significant part of Rh is reduced to the metallic state during the treatment at high temperatures in vacuum. To prevent the formation of metallic Rh during the treatment in vacuum the following studies have been performed with samples calcined in O_2.

3.2. SOLID-STATE EXCHANGE IN OXYGEN

As in the case of the treatment in vacuum the intensities of both bands attributed to the acid OH groups decreased when the calcination had been performed at temperatures higher than 400°C. The intensity of the HF band decreases by 0, 14

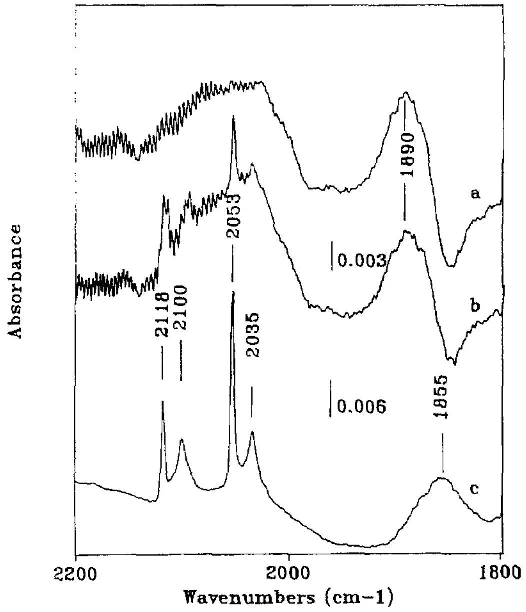

Fig. 1. IR spectra in the region of the CO stretching vibrations of $RhCl_3$/DAY treated in vacuum at 580°C after interaction with CO at r.t. (a), at 150°C for 15 min (b), and at 150°C for 2 h (c). Note the different absorbance scales.

and 19% after calcination at 400, 500 and 600°C, respectively. Corresponding decreases for the LF bands are 0, 19, 24%.

To discuss the mechanism of ion exchange with dealuminated zeolites one has to consider that the exchange and location of polyvalent cations at positions in the supercages is rather unlikely due to the large distances of the Al ions in highly dealuminated zeolites. The three-valent Rh can enter the cation positions, therefore, only in form of complex cations (eqs. (1) and (2)), similarly as proposed by Kucherov et al. [2] for oxidic species of Cr, Mo, and V:

$$(\mathrm{Si{-}O{-}Al}){-}\mathrm{H} + \mathrm{RhCl_3} \rightarrow (\mathrm{Si{-}O{-}Al}){-}\mathrm{RhCl_2} + \mathrm{HCl}\,, \qquad (1)$$

$$(\mathrm{Si{-}O{-}Al}){-}\mathrm{H} + \mathrm{RhCl_3} + \tfrac{1}{2}\mathrm{O_2} \rightarrow (\mathrm{Si{-}O{-}Al}){-}\mathrm{RhO} + \mathrm{HCl} + \mathrm{Cl_2}\,. \qquad (2)$$

The analysis of the OH bands points to an exchange degree of less than 25% for the sample calcined at 600°C. An estimation of the amount of the Rh exchanged into cationic positions showed that only 5% took place in the exchange. Most part of Rh is located at the outer surface of the zeolite. One may speculate on the nature of the Rh compound formed during calcination at different temperatures. The final product should be Rh_2O_3 but oxychlorides and/or hydroxychlorides could not be excluded as by-products especially at 400°C.

Treatment of the samples with CO results in the appearance of absorption bands in the carbonyl stretching region between 2200 and 1700 cm^{-1} and changes in the OH stretching region. In fig. 2 the infrared absorption bands are shown for the sample calcined at 600°C in the OH stretching region (fig. 2A) and in the CO stretching region (fig. 2B), after treatment with CO at r.t. (spectrum a), at 100°C (spectrum b), and at 150°C (spectrum c). The absorption bands at 2118 and 2053 cm^{-1} increase in intensity with rising interaction temperature in CO. These bands are assigned to a well-defined $Rh(CO)_2^+$ structure in highly dealuminated Y zeolites located in the vicinity of the Si–O–Al groups [13,14]. The bands near 2100 and 2035 cm^{-1} hardly change with temperature. Simultaneously with the appearance and the development of the narrow bands at 2118 and 2053 cm^{-1} a loss of OH groups proceeds as indicated by the decrease of the bands at 3631 and 3568 cm^{-1} (fig. 2A). Obviously, an additional ion exchange has occurred during the formation of the well-defined $Rh(CO)_2^+$ species. The influence of CO on the ion exchange of rhodium into dealuminated Y zeolites has been studied, therefore, in more detail also for the other samples.

3.3. SOLID-STATE EXCHANGE IN THE PRESENCE OF CO

Similarly as demonstrated for the sample calcined at 600°C, the treatment with CO causes for all samples a decrease of the intensity of both the HF- and LF-bands. The extent of OH consumption increases as the reaction temperature is increased (fig. 3). The exchange of protons reaches more than 50% in the presence of gaseous

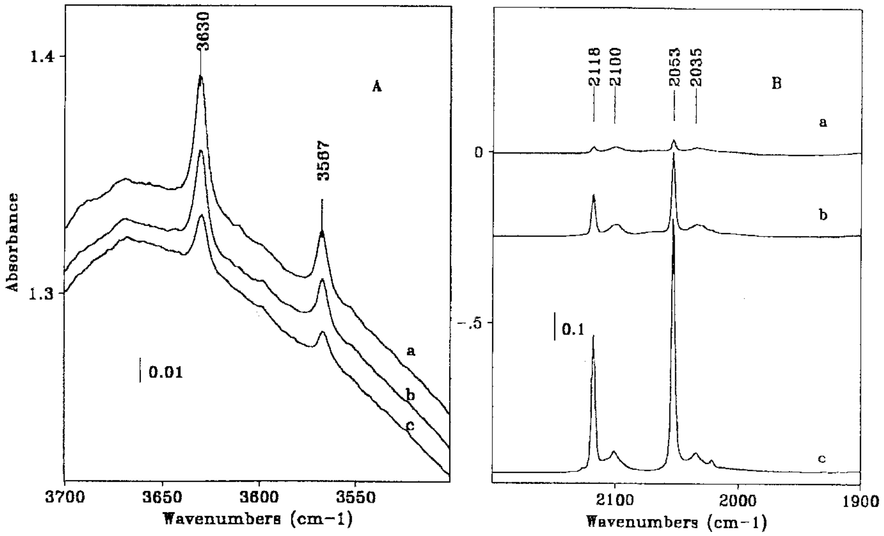

Fig. 2. IR spectra of the samples $RhCl_3$/DAY calcined at 600°C. (A) Spectra in the region of the OH stretching vibrations after exposure to CO at r.t. (a), at 100°C (b), at 150°C (c). (B) Spectra in the region of the CO stretching vibrations (assignment as in A).

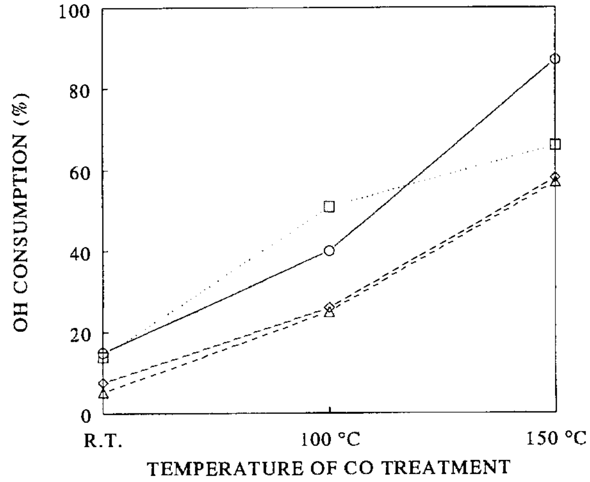

Fig. 3. Consumption of the acid OH groups in dependence on the temperature of interaction with CO for $RhCl_3$/DAY calcined at 400°C (○), 500°C (△), 600°C (◇) and at 400°C followed by reduction with hydrogen at 300°C (□).

CO, i.e. significantly more than by calcination at higher temperatures in vacuum or in oxygen. At the same time the intensities of the doublet at 2118 and 2053 cm^{-1} increases (fig. 4A), whereas the intensities of the bands at 2100 and 2035 cm^{-1} do not significantly change with rising reaction temperature (fig. 4B). Fig. 4 shows furthermore a decrease of the intensities of both bands with increasing calcination temperature.

Let us first discuss the possibility of the formation of well-defined dicarbonyls with Rh already exchanged and located at cation sites. As described above the formation and development of the narrow bands attributed to the well-defined dicarbonyl strongly increase with rising reaction temperature. The formation of Rh dicarbonyls has been reported by Primet et al. [19] on NaY zeolite exchanged with $[Rh(NH_3)_5Cl]Cl_2$ following the equation

$$\begin{aligned}(\text{Si–O–Al})_3\text{– Rh(III)} + 3\text{CO} + \text{H}_2\text{O} &\rightarrow (\text{Si–O–Al})\text{–Rh(I)(CO)}_2 \\ &+ \text{CO}_2 + 2(\text{Si–O–Al})\text{–H},\end{aligned} \tag{3}$$

i.e. the reduction of Rh(III) is accompanied by the formation of CO_2 and acid OH groups. In our case, the formation of the dicarbonyl should proceed by reduction of the complex ion according to the following equation without production as well as consumption of protons:

$$(\text{Si–O–Al})\text{–RhO} + 3\text{CO} \rightarrow (\text{Si–O–Al})\text{–Rh(I)(CO)}_2 + \text{CO}_2\,. \tag{4}$$

It seems, however, that protons are consumed in our experiment during the formation of the dicarbonyl. Moreover, with exchanged Rh as the source of the well-

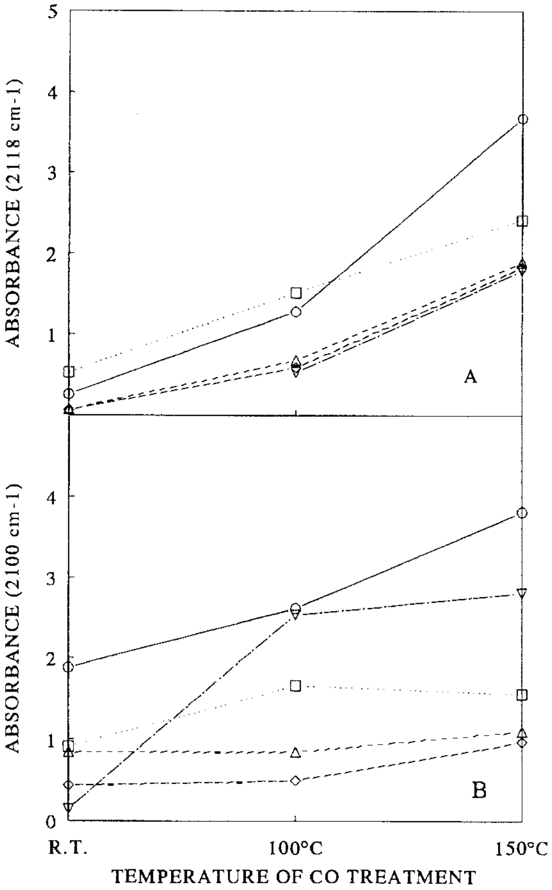

Fig. 4. Intensities of the bands at 2118 cm^{-1} (A) and 2100 cm^{-1} (B) in dependence on the temperature of interaction with CO for $RhCl_3$/DAY non-calcined (∇), calcined at 400°C (○), 500°C (△), 600°C (◇) and at 400°C followed by reduction with hydrogen at 300°C (□).

defined dicarbonyl it should be expected that its formation depends on the amount of rhodium located at cation positions. Our results show a rather reverse behaviour (see fig. 4A). The highest amount of Rh dicarbonyl is obtained with the sample calcined at 400°C, i.e. with the sample with almost no ion exchange. A reduction of exchanged Rh should be accompanied by an increase of the intensity of the IR bands of the acid hydroxyls, as has been really found by Wong et al. [20]. With the samples studied in the present work the intensity of the bands of the acid OH groups remains unchanged after reduction. This is an additional argument that an ion exchange has not occurred during calcination at 400°C. These results show that Rh dicarbonyl is formed with rhodium located originally not at the cation positions in the zeolite micropores.

This conclusion has been supported by an experiment with a non-calcined mixture of $RhCl_3$ and DAY. The result is shown in fig. 5. Treatment with CO at r.t. shows only a band at 2145 cm^{-1} (spectrum a), due to CO adsorbed on Rh^{3+}. With increasing temperature the narrow bands at 2118 and 2053 cm^{-1} appear (spectrum b) and grow distinctly by further increase of the temperature to 150°C (spectrum c), while the other bands have not been changed in intensity. This result clearly shows that the dicarbonyl has been formed from Rh^{3+} ions located outside of the zeolite. It is well known that $[Rh(CO)_2Cl]_2$ and $Rh(CO)_2^+$ can be formed by the reaction of $RhCl_3$ with CO at elevated temperatures. If the same non-calcined mixture has been reduced before interaction with CO, one would expect the formation of large Rh particles, which are not able to form Rh dicarbonyls with CO. Spectrum a of fig. 6 shows only very small bands at 2091, 2023, and 1880 cm^{-1}, indicating CO adsorbed as bridged bonded CO and in form of a $Rh(CO)_2^+$ on the outer surface resulting probably from a small amount of unreduced Rh. Spectrum b of fig. 6 demonstrates the different behaviour of the non-reduced sample in comparison to the reduced one. As expected, $Rh(CO)_2^+$ has not been formed in this experiment.

Reduction of the sample previously calcined at 400°C results, on the other hand, in a completely different behaviour. By interaction of CO with the reduced sample bands of comparable intensities as in the case of the oxidized one have been

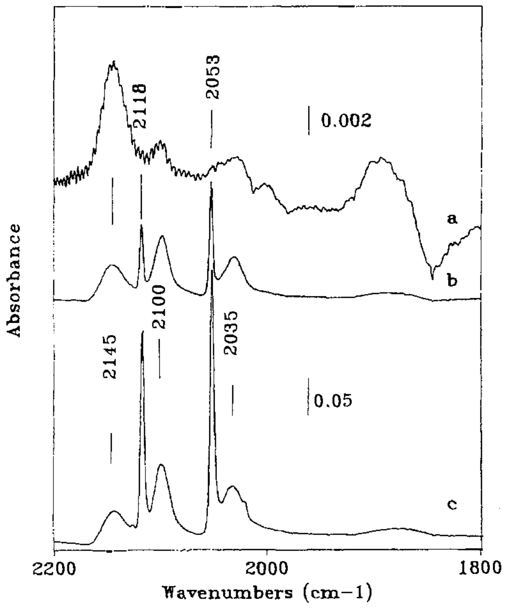

Fig. 5. IR spectra in the region of the CO stretching vibrations of the non-calcined sample $RhCl_3$/DAY after interaction with CO at r.t. (a), 100°C (b), and 150°C (c). Note the different absorbance scales.

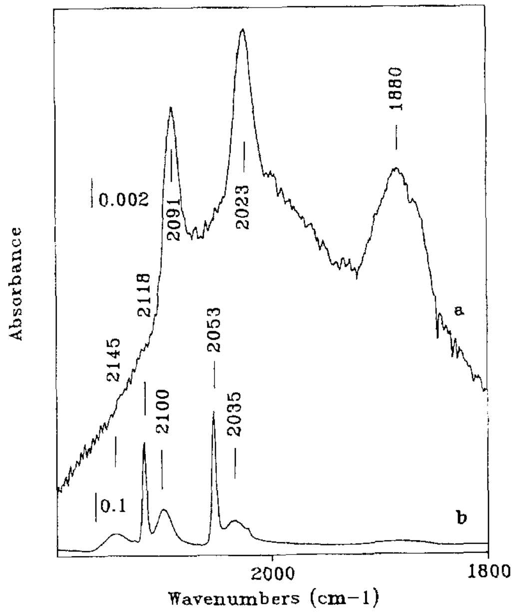

Fig. 6. IR spectra in the region of the CO stretching vibrations of the non-calcined, but reduced sample $RhCl_3$/DAY after interaction with CO at 150°C (a). For comparison, the corresponding spectrum (fig. 5c) of the non-reduced sample is included (b). Note the different absorbance scales.

observed (see fig. 7). Besides the twin bands, a broad band with maximum near 2040 cm^{-1} is seen assigned to linearly bonded CO on metallic Rh. Furthermore, a broad band located at 1880 cm^{-1} in presence of gaseous CO and shifted to 1855 cm^{-1} during desorption points to bridged bonded CO on metallic particles of Rh on the outer surface of the zeolite. The band at 2100 cm^{-1} is also observed, whereas the band at 2035 cm^{-1} may be masked by the band at 2040 cm^{-1}. Bands of CO adsorbed on three-valent Rh are absent. The intensities of the bands attributed to CO on metallic Rh are independent of the reaction temperature but the intensity of the twin bands increases in a similar way as in the case of the oxidized sample (fig. 7B, spectra a–c). The formation of the well-defined dicarbonyl is accompanied by a decrease of the intensities of the acid hydroxyl groups (fig. 7A) as already found for the only calcined samples. In this case, however, the consumption of protons could be explained also by the participation of acid hydroxyls in the oxidative disruption of small Rh particles [9,10,12,14,20] according to

$$Rh^0 + 2CO + (Si{-}O{-}Al){-}H \rightarrow (Si{-}O{-}Al){-}Rh(CO)_2 + \tfrac{1}{2}H_2 . \qquad (5)$$

Figs. 8A and 8B demonstrate the connection between the formation of the well-defined dicarbonyls and the simultaneous decrease of the intensities of the hydroxyl bands. Obviously, there is a linear correlation between the intensities of the bands at 2118 and 2053 cm^{-1} and the consumption of the acidic OH groups,

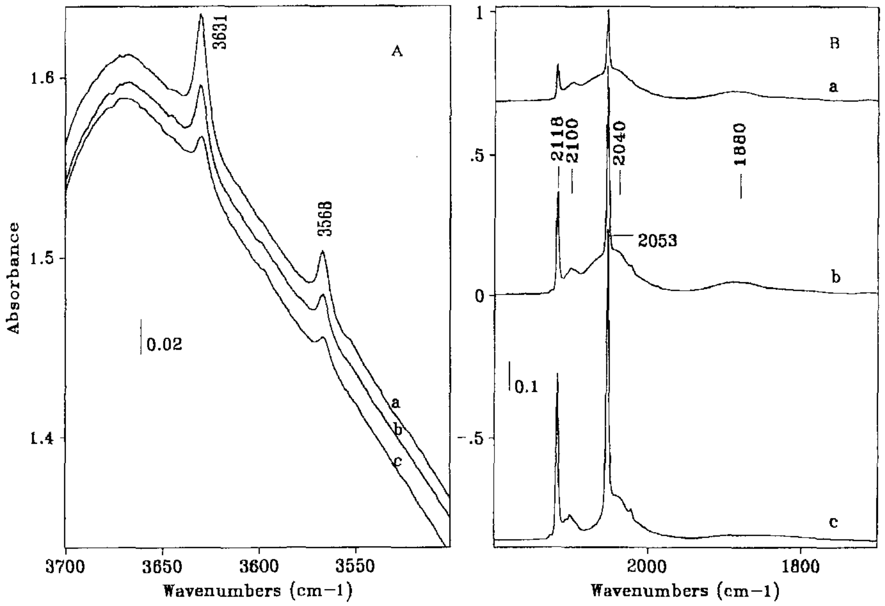

Fig. 7. IR spectra of the reduced sample previously calcined at 400°C. (A) Spectra in the range of the OH stretching vibrations after interaction with CO at r.t. (a), at 100°C (b), and at 150°C (c). (B) Spectra in the range of the CO stretching vibrations (assignment as in A).

independent of both the calcination temperature and the temperature of the interaction of the samples with CO. Even the additionally reduced sample fits this correlation.

In order to explain the results described above a model is postulated which assumes that the formation of $Rh(CO)_2^+$ proceeds on the outer surface of the zeolite by interaction of CO with Rh_2O_3 and/or Rh-oxychloride formed during calcination according to

$$Rh_2O_3 + 6CO \rightarrow 2Rh(I)(CO)_2^+ + 2CO_2 + O^{2-} . \qquad (6)$$

The dicarbonyl cation can migrate to the protons in the zeolite cages, where the exchange reaction proceeds in accordance to

$$2(Si{-}O{-}Al){-}H + 2Rh(CO)_2^+ + O^{2-} \rightarrow 2(Si{-}O{-}Al){-}Rh(I)(CO)_2 + H_2O . \qquad (7)$$

The high mobility of the $Rh(CO)_2^+$ was already proposed from XPS measurements by Takahashi et al. [21], who described a migration of the dicarbonyl from the outer surface of a Rh loaded Y zeolite by exposure to CO in the temperature range of 80–160°C and the reverse process in presence of H_2 or H_2O.

With increasing calcination temperature the Rh oxide particles grow and as a consequence their reactivity to form a dicarbonyl is declined resulting in a lower intensity of the twin bands. Reduction of dispersed Rh_2O_3 with H_2 yields highly dis-

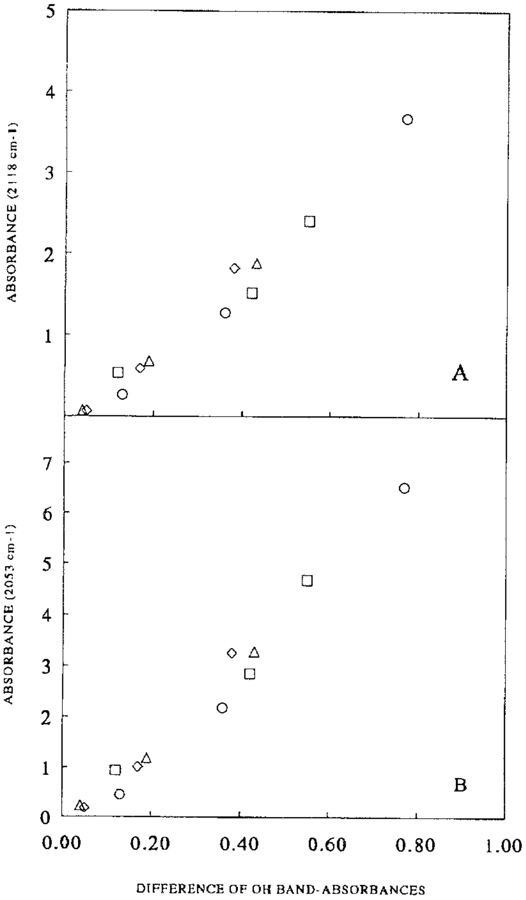

Fig. 8. Intensities of the bands at 2118 cm^{-1} (A) and 2053 cm^{-1} (B) in dependence on the consumption of the acid OH groups for $RhCl_3$/DAY calcined at 400°C (○), 500°C (△), 600°C (◇) and at 400°C followed by reduction with hydrogen at 300°C (□) after interaction with CO at different temperatures.

persed metal particles, which react with CO and protons to the dicarbonyl located in the zeolite cages. The disruption of Rh–Rh bonds of small Rh crystallites could occur also on the outer surface of the zeolite and the dicarbonyl formed may participate in the ion exchange as in the case of the non-reduced samples. On the other hand, CO is unable to break the Rh–Rh bonds of large Rh crystallites, which are formed during the reduction of $RhCl_3$, i.e. the reduction of non-calcined samples. In the case of the sample which was neither calcined nor reduced, the first step of the interaction of CO with the $RhCl_3$/DAY mixture could be the formation of $Rh(CO)_2^+$ or of $[Rh(CO)_2Cl]_2$ on the outer surface of the zeolite as indicated by the appearance of absorption bands near 2100 and 2035 cm^{-1}. A subsequent migration of the carbonyl species into the micropores of the zeolite results also in this case in the ion exchange and the formation of well-defined Rh dicarbonyl at cation positions.

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