Well-defined carbonyl and dinitrogen complexes of ruthenium supported on dealuminated Y zeolite. Analogies and differences to the homogeneous case

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Abstract

The surface chemistry of Ru supported on dealuminated Y zeolite with CO and N_2 has been studied by FTIR spectroscopy and ligand exchange with ^{13}CO and $^{15}N_2$ combined with related force field calculations. Two Ru tricarbonyls, one with a facial and one with a meridional structure, are formed in the zeolite matrix, and their mutual conversion has been studied. The chemistry of these complexes seems to be a surface analog of the complex chemistry in solution. Upon decarbonylation well-defined di- and monocarbonyls could be identified. The monocarbonyl is highly reactive and forms well-defined dinitrogen complexes. A bis-dinitrogen, $[Ru^{II}(N_2)_2]^{2+}$, and a mixed carbonyl dinitrogen complex, $[Ru^{II}(CO)(N_2)]^{2+}$, are found to be stable in a nitrogen atmosphere at 523 K. In addition to these complexes, Ru forms further dinitrogen complexes stable at room temperature. In particular, a *trans*-dicarbonyl dinitrogen complex, $[Ru^{II}(CO)_2(N_2)]^{2+}$, is stable even in the presence of CO and the absence of N_2 in the gas phase. The surface dinitrogen complexes do not have precedents in the Ru complex chemistry. They are stabilised obviously by the zeolite matrix and bound probably at the isolated cation sites. The wavenumbers and force constants of the dinitrogen ligands indicate a stronger bonding to the metal compared to Rh and, consequently, a higher activation of the attached molecular nitrogen. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

From IR-spectroscopic studies, it is evident that well-dispersed Ru is able to form a number of different surface species, depending on the support, the dispersion, the pretreatment, the experimental conditions etc. Surface carbonyls with one to three carbonyl groups per Ru atom and with the metal in different oxidation states have been suggested to exist, sometimes simul-

taneously, on the surface. The tendency of ruthenium to form polynuclear carbonyl clusters increases additionally the number of possible surface complexes. Moreover, the IR bands of the surface species are often rather broad and the overlapping of them complicates an unambiguous assignment. Clearly, a better knowledge of well-defined Ru carbonyl complexes on the surface would be helpful.

The interaction of molecular nitrogen with Ru has attracted much attention since the discovery of the first dinitrogen complex $[Ru^{II}(NH_3)_5(N_2)]^{2+}$ in 1965 [1]. This and numerous dinitrogen complexes obtained in the following

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also with other metals have been studied particularly in connection with nitrogen fixation models [2–6].

The interaction of molecular nitrogen with supported transition metals is usually weak. Using IR spectroscopy, an adsorption on supported Ru has been found either at low temperature (123 K) [7] or with Ru on certain supports (Al_2O_3, MgO) [8,9]. Depending on the support, the promoter and the pre-treatment, N_2-stretching bands in a broad region between 2214 and 1910 cm^{-1} have been obtained.

On the other hand, there are a few reports on the formation of dinitrogen complexes with metals supported on zeolites. Monodinitrogen complexes have been found with Cu^I in mordenite [10–12] and in ZSM-5 [13,14].

With rhodium supported on dealuminated Y zeolites (DAY, US-Ex), we obtained recently [15,16] well-defined surface complexes of Rh^I with molecular nitrogen, that are stable in a flow of nitrogen at temperatures up to 523 K. The dinitrogen complexes were characterised as a Rh-bis-dinitrogen complex $[Rh^I(N_2)_2]^+$ and a mixed carbonyl dinitrogen complex $[Rh^I(CO)N_2]^+$, most probably attached to the zeolite framework oxygen atoms at the isolated Al sites. Related dinitrogen surface species have been postulated to exist also on Rh/Al_2O_3 during the interaction of CO and N_2 in the presence of ultraviolet radiation [17]. As we will show in the present work, similar complexes are formed also with Ru/DAY, but there are also significant differences as compared to Rh/DAY [18]. [1]

2. Experimental

The support DAY (DEGUSSA, Germany) is a Y zeolite with a Si:Al ratio ≥ 100, dealuminated by exchange of the Al atoms in the framework by treating the NaY with $SiCl_4$. The

sample Ru/DAY (1 wt.% Ru) has been prepared by impregnation of the support with the appropriate amount of $RuCl_3$ in ethanolic solution and drying the sample at 353 K in air. Additional pretreatment was performed directly in the infrared cell. It consisted usually in a carbonylation in a flow of 5% CO/Ar at 523 K. A chlorine free sample (1 wt.% Ru) has been obtained by impregnation of the support with $Ru_3(CO)_{12}$ in ethanolic solution and drying the sample at 333 K in air. Regarding the dinitrogen complexes, identical results have been obtained.

Transmission IR studies were performed with self-supported wafers using a special infrared cell made from stainless steel for in-situ measurements up to 673 K and 5000 kPa, connected to a gas flowing system, which allows a fast variation of the feed gas. The gas flow through the cell was controlled using electronic flow controllers. The gases used were of high purity (AGA Gas) and were additionally purified by OXYSORB units (Messer Griesheim). For the isotopic exchange, ^{13}CO (99%, Linde) and $^{15}N_2$ (98%, Chemotrade) have been used. The spectra were recorded with a Perkin Elmer Paragon 1000 FTIR spectrometer at a resolution of 2 cm^{-1}. To obtain a sufficient signal-to-noise ratio, 10–50 scans were coadded. The spectra shown in the figures are corrected for the background of the sample without surface species.

Force field calculations were performed with an energy-separated force field taking into account the CO- and N_2-stretching force constants and constants for the interaction between the ligands [19]. The force and interaction constants were optimised with a force field calculation program [20] using experimentally observed wavenumbers.

3. Results and discussion

3.1. Ruthenium tricarbonyls. Isomeric facial and meridional structures

Fig. 1a shows the IR spectrum of the Ru/DAY sample after interaction with CO at tem-

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[1] Some of the results presented in Ref. [18] were the subject of a preliminary communication.
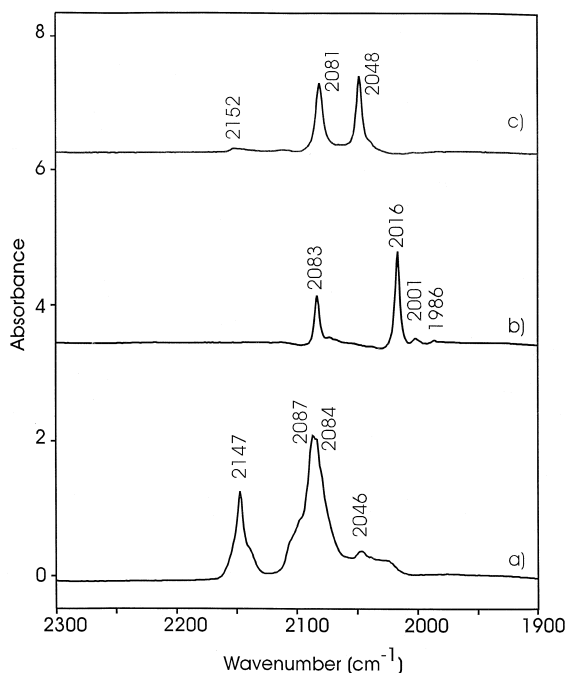
Fig. 1. Infrared difference spectra of Ru/DAY in the carbonyl stretching region after carbonylation with 5% CO/Ar at 523 K (a); after a subsequent decarbonylation in 50% H_2/N_2 at 573 K (b); after a subsequent recarbonylation with 5% CO/Ar at 423 K (c).

peratures up to 523 K. This spectrum with bands at 2152, 2091 and 2086 cm^{-1} (at 300 K) has been assigned previously [21] to an Ru fac-tricarbonyl with slightly distorted C_{3v} structure.

A decarbonylation of this tricarbonyl results in an IR spectrum, that can be assigned (see next paragraph) to a dicarbonyl (Fig. 1b). As the results of a subsequent recarbonylation at temperatures up to 423 K, a new spectrum (Fig. 1c) is found with strong carbonyl bands at 2081 and 2048 cm^{-1} and a weaker one at 2152 cm^{-1}. This spectrum transforms at higher temperatures under CO into the spectrum of the starting Ru fac-tricarbonyl. A closer inspection of a series of experiments shows that the intensities of the three bands at 2154, 2081, 2049 cm^{-1} (at 300 K) are correlated. As the new species is formed upon addition of CO to a dicarbonyl, it is reasonable to assume a polycarbonyl with more than two carbonyl ligands and the intensity

pattern with a weak intensity of the high-frequency band and similar intensities of two low frequency bands points to a tricarbonyl with a meridional structure. Different to the facial tricarbonyl structure, where the three CO ligands are nearly identical in a C_{3v} symmetry, in this structure, two CO ligands are trans to each other and the third CO group is in a cis-position. As result of the trans-CO position, the symmetric CO-stretching at high frequency $(A_1)_1$ has a very low intensity in the infrared spectrum [19].

To confirm the assignment of the triplet at 2154, 2081 and 2049 cm^{-1} to a surface mer-tricarbonyl, we performed a ligand exchange with ^{13}CO and calculated the corresponding wavenumbers in an energy-separated force field for different structure models. Only for the mer-tricarbonyl structure, we obtained a satisfactory agreement between calculated and observed values. All other structure models of di- and tricarbonyls failed to reproduce the observed sequence of IR bands. It should be noted that the ligand exchange is fast at room temperature, whereas the related exchange of the surface fac-tricarbonyl requires a temperature of 423 K or higher.

In the complex chemistry of Ru several mer-tricarbonyls are known and the mutual conversion of the facial and meridional isomers of $[Ru^{II}(CO)_3I_3]^-$ has been followed in detail by Zoeller using IR and ^{13}C NMR spectroscopy [22]. The fac-$[Ru^{II}(CO)_3I_3]^-$ with characteristic IR bands at 2097 and 2026 cm^{-1} is first decarbonylated into an intermediate dimeric dicarbonyl (2033, 1969 cm^{-1}), that can be recarbonylated under an atmosphere of CO to the mer-$[Ru^{II}(CO)_3I_3]^-$ with IR bands at 2112 (w), 2041 (vs) and 2012 (s) cm^{-1}. The mer-$[Ru^{II}(CO)_3I_3]^-$, on the other hand, can be converted directly into the fac-isomer by heating under a CO atmosphere. In a recent structural and theoretical work on related fac- and mer-tricarbonyl complexes of Mn and Re, it was shown that this relationship between these structural isomers are of general importance [23].

The behaviour of the tricarbonyls of Ru on DAY seems to be a direct surface counterpart to the complex chemistry in solution. This analogy of the surface carbonyls to related Ru complexes suggests an oxidation state of $+2$ also for the surface species. An oxidation state of $+1$ as proposed for the related Rh complexes on the surface [15,16,24,25] would be rather unusual for Ru. The cation sites in dealuminated zeolites are, on the other hand, isolated each from other and can compensate for only one charge. Different to the monovalent Rh^I complexes, the Ru^{II} species require an additional charge-compensating ligand. That might by an extra-framework hydroxy group, similar as proposed for the localisation of Cu^{II} in ZSM-5 [26], or a defect site available or created during the complex formation near the cation sites.

In Scheme 1, the mutual transformation of the isomeric surface carbonyls is shown schematically. The carbonyl wavenumbers of the surface complexes are shifted by 50–65 cm^{-1} to higher values, compared to the complexes with iodide ligands. The situation is similar as for the Rh complexes, for which the zeolite-attached dicarbonyls have wavenumbers 70–90 cm^{-1} higher than the corresponding iodide complexes [24,25]. This blue shift is due to the higher electronegativity of the zeolite framework oxygen's compared to the iodide ligands.

3.2. Decarbonylation. Ru di- and monocarbonyls

A controlled decarbonylation of the Ru tricarbonyl in an inert atmosphere or in a hydro-
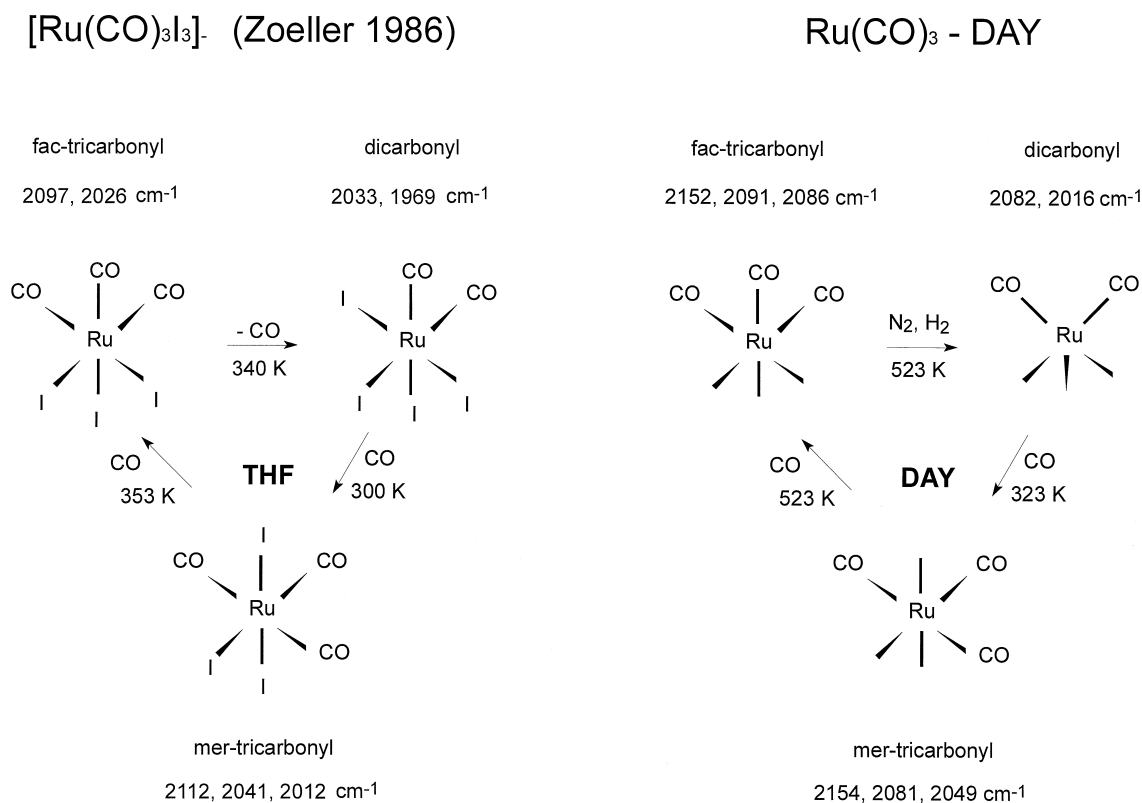
Scheme 1.

gen-containing gas flow at temperatures higher 473 K results primarily in an IR spectrum, that resembles that of a dicarbonyl (Fig. 1b). If the decarbonylation is performed starting with a tricarbonyl obtained from a mixture of ^{12}CO and ^{13}CO, a dicarbonyl is formed with different isotopic composition. A corresponding force field calculation confirms the assignment to a dicarbonyl. The Ru dicarbonyl seems to be similar to that of rhodium [24,25], but with significant lower wavenumbers at 2082 and 2016 cm^{-1} as compared with Rh/DAY at 2115, 2050 cm^{-1} (at 523 K). As for the Rh dicarbonyl, intensity and sharpness of the bands allow the resolution of ^{13}CO satellite band at 1986 cm^{-1} (at 573 K) even with the 1.1% ^{13}CO from natural abundance (Fig. 1b). From the intensity ratio between the antisymmetric and symmetric CO-stretching mode, a bond angle of $113 \pm 1°$ can be estimated [19]. This value is significantly higher than the 106° estimated for the Rh dicarbonyl [24,25].

For rhodium on dealuminated Y zeolite, it was shown [15,16] that a partial decarbonylation of the stable surface dicarbonyl to form a reactive monocarbonyl as an intermediate is a crucial step to obtain dinitrogen complexes. The same observation was made by Wovchko and Yates [17], who found that an intermediate Rh monocarbonyl obtained during UV radiation is the prerequisite to the formation of dinitrogen surface species on Rh/Al$_2$O$_3$.

The well-defined Ru dicarbonyl with wavenumbers at 2082 and 2016 cm^{-1} (at 523 K) as described above undergoes in flowing hydrogen at 523–573 K a further partial decarbonylation to a monocarbonyl with a carbonyl band at 2036 cm^{-1}. Fig. 2 shows the corresponding difference spectra in the carbonyl stretching region. They clearly demonstrate the formation of the monocarbonyl and the simultaneous disappearance of the dicarbonyl. The isobestic points at 2047 and 2027 cm^{-1} indicate the transformation on the same surface site. It should be noted that, as the dicarbonyl, also the Ru monocarbonyl has a smaller stretching
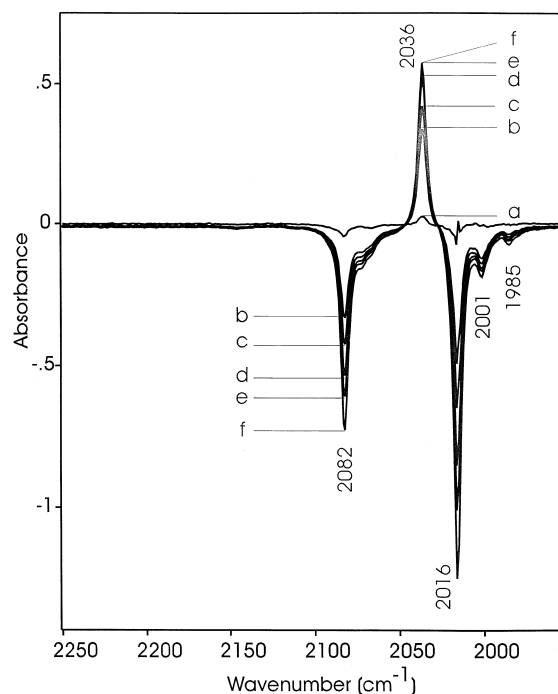

Fig. 2. Infrared difference spectra in the carbonyl stretching region obtained at 523 K during the interaction of 70% H$_2$/N$_2$ for 30 (a), 60 (b), 90 min (c) and of pure H$_2$ for 30 (d), 60 (e), 150 min (f) with a Ru dicarbonyl on the surface.

wavenumber, than that obtained with the corresponding Rh species at 2090 cm^{-1} [15,16].

3.3. Dinitrogen complexes on the surface

Fig. 3 shows the difference-spectra in the N≡N and C≡O stretching region obtained with the monocarbonyl as shown in Fig. 2 after the gas flow has switched from hydrogen to pure nitrogen at 523 K. The appearance of bands at 2218, 2207 and 2173 cm^{-1} with the expected shift of 72–73 cm^{-1}, if ^{15}N$_2$ is used instead of ^{14}N$_2$ (spectrum 3b), clearly indicates the formation of dinitrogen compounds. Simultaneously, the band of the intermediate monocarbonyl at 2036 cm^{-1} disappears and new bands in the carbonyl stretching region are growing. The bands at 2082 and 2016 cm^{-1} are due to the reversibly formed dicarbonyl, whereas the new band at 2023 cm^{-1} should be assigned to a new species. If using a mixture of ^{12}CO and ^{13}CO
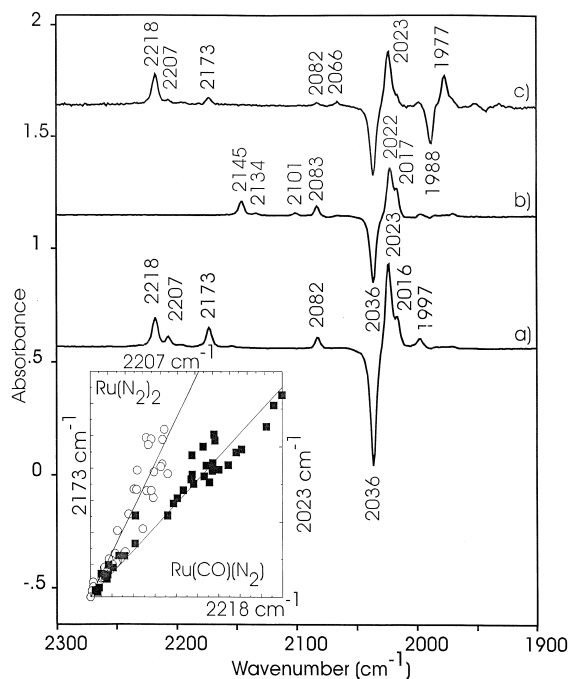
Fig. 3. Infrared difference spectra in the carbonyl and dinitrogen stretching region obtained at 523 K after switching the gas flow from hydrogen to N_2 (a); after a subsequent exchange with $^{15}N_2$ (b); as (a), but with carbonyls formed from a mixture of ^{12}CO and ^{13}CO (c). The insert shows the correlation between the integrated absorbances at 2207 and 2173 cm^{-1} (open circles, N_2-stretching; $N = 41$, $R^2 = 0.871$, slope $= 2.25 \pm 0.08$) and between the integrated absorbances at 2218 and 2023 cm^{-1} (solid square, N_2- and CO-stretching; $N = 38$, $R^2 = 0.954$, slope $= 3.10 \pm 0.06$).

(spectrum 3c), the two negative bands at 2036 and 1988 cm^{-1}, due to the intermediate monocarbonyl, are replaced by only two bands at 2023 and 1977 cm^{-1}, i.e., a new monocarbonyl has been formed. An analysis of the integrated absorbances of a series of experiments between 423 and 523 K and 100–400 kPa N_2 pressure (insert in Fig. 3) revealed a correlation of the bands at 2218 and 2023 cm^{-1} and also of the bands at 2207 and 2173 cm^{-1}. Thus, at a temperature of 523 K, the picture seems to be similar to that found for Rh/DAY [15,16] and we assign the first pair of bands to a mixed carbonyl dinitrogen complex, $[Ru^{II}(CO)(N_2)]^{2+}$, and the latter one to a bis-dinitrogen species $[Ru^{II}(N_2)_2]^{2+}$. To confirm this assignment additionally, we performed a partial ligand exchange

with $^{15}N_2$ and Fig. 4 shows the corresponding IR bands in the N_2-stretching region. A comparison of their wavenumbers with those obtained in a related force field calculation proves the assignment taken. It might be worth to note that an exchange of $^{14}N_2$ for $^{15}N_2$ in the mixed carbonyl dinitrogen complex results also in a small, but significant change in the CO-stretching from 2023 to 2022 cm^{-1} (Fig. 3b). This is due to the weak interaction of the two ligands in the mixed complex.

As for the pure carbonyls, the carbonyl and dinitrogen bands of the dinitrogen complexes are at lower wavenumbers than those of their corresponding Rh analogs. This indicates a stronger bond between the metal and the ligands due to a stronger π-backbonding and, consequently, a stronger activation of the dinitrogen ligand.

The bond angle between the two dinitrogen ligands in the bis-dinitrogen complex $[Ru^{II}$-
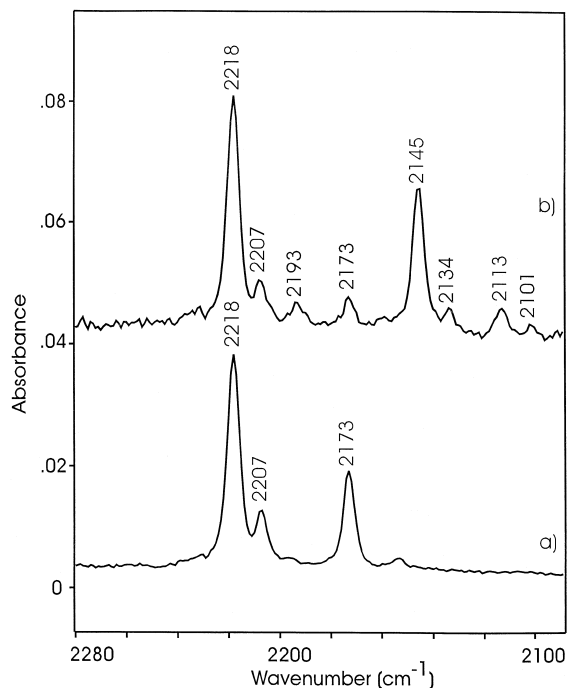

Fig. 4. IR spectra in the dinitrogen stretching region after formation of the dinitrogen complexes at 523 K with $^{14}N_2$ (a); and after interaction with $^{14}N_2$:$^{15}N_2$ ca. 60:40 (b).

$(N_2)_2]^{2+}$, as estimated from the slope of the correlation between the N_2-stretching modes in Fig. 3, is ca. 113° similar to the 112°, as found [15,16] for $[Rh^I(N_2)_2]^+$. As found for Rh/DAY, the force constant of the N_2-stretching is higher in the mixed complex $[Ru^{II}(CO)(N_2)]^{2+}$ than in the bis-dinitrogen complex $[Ru^{II}-(N_2)_2]^{2+}$. Just the opposite has been found for the CO-stretching: in the dicarbonyl, $k(CO)$ is higher than in the mixed complex. These results are explained as for Rh/DAY [15,16] by the stronger π-acceptor ability of CO compared with the dinitrogen ligand.

The analogy of Ru and Rh supported on dealuminated zeolites is, however, restricted to the properties at high temperature (higher than 423 K). The dinitrogen species found for Rh/DAY at 523 K were the same as those found at 300 K [15,16]. On the other hand, cooling down the dinitrogen species of Ru/DAY, new IR bands are growing and became dominating at 323 K (Fig. 5). They are several new bands in the N_2-stretching region (2257, 2238 and 2205 cm^{-1}) and, simultaneously, a new strong band in the carbonyl stretching region at 2039 cm^{-1} is growing. An analysis of the integrated absorbances (insert in Fig. 5) indicates the formation of a new mixed carbonyl dinitrogen complex with wavenumbers at 2257 and 2039 cm^{-1} and a ligand exchange with ^{13}CO and $^{15}N_2$ confirms this assignment. Regarding the significantly higher wavenumbers of both the N_2- and the CO-stretching compared to the related high-temperature mixed complex, and also the different intensity ratio's as expressed by the slopes of the corresponding correlation's (Figs. 3 and 5), a different structure of the complexes should be expected. A different attachment to the zeolite framework might be responsible for the difference.

The new N_2-stretching bands at 2238 and 2205 cm^{-1} at 300 K could be due to a new bis-dinitrogen complex, but an unambiguous assignment is not possible, because of several weak overlapping bands in the isotopic exchange experiments.
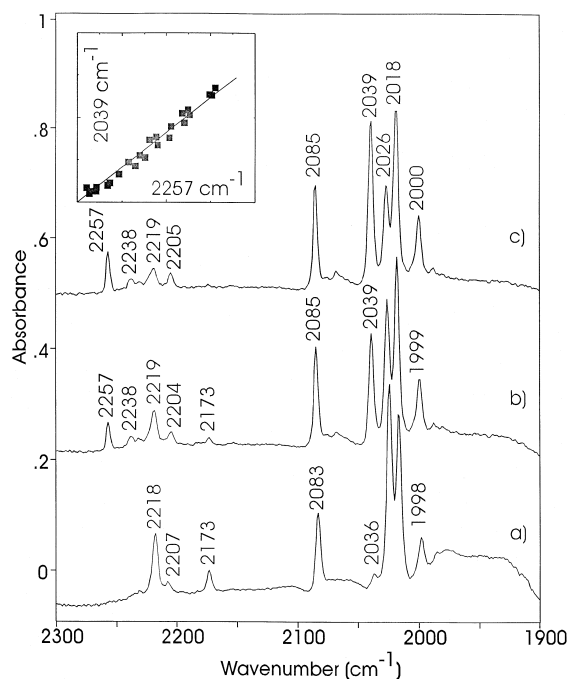

Fig. 5. IR spectra in the carbonyl and dinitrogen stretching region after the formation of the dinitrogen complexes in a flow of N_2 at 473 K (a); and decreasing the temperature to 358 K (b) and 323 K (c). The insert shows the correlation between the integrated intensities of the N_2-stretching at 2257 and the CO-stretching at 2039 cm^{-1} ($N = 24$, $R^2 = 0.980$, slope = 4.11 ± 0.07).

There is another significant difference with respect to Rh/DAY. Whereas the Rh dinitrogen complexes are very sensitive towards traces of CO in the gas phase and convert immediately into the stable dicarbonyl, the Ru dinitrogen species transform at 323 K with CO in the gas phase into a new stable dinitrogen complex with an intensive $N\equiv N$ stretching band at 2231 cm^{-1} (Fig. 6a). The integrated intensity of this band is correlated to a new strong carbonyl band at 2061 cm^{-1} (insert in Fig. 6) and the appearance of a weak band at 2129 cm^{-1} seems to be also related to the new dinitrogen stretching band. From the other carbonyl bands those at 2153, 2081, and 2049 cm^{-1} are of the mer-tricarbonyl formed at this conditions from the Ru dicarbonyl (vide supra). As shown in Fig. 6b, the new dinitrogen species is stable even in a flow of CO in Ar without any N_2 in the gas phase. Only at increasing temperatures (over 323 K) it
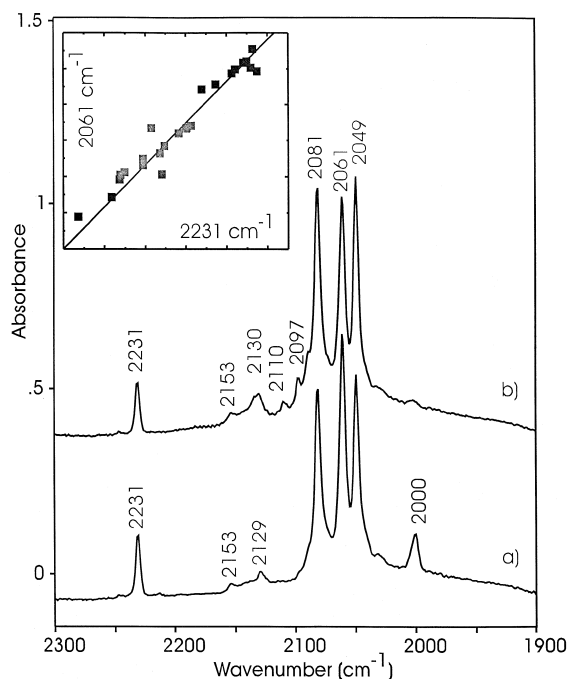
Fig. 6. IR spectra in the carbonyl and dinitrogen stretching region after the formation of dinitrogen complexes as in Fig. 5(c) and subsequent admission of 1% CO to the N_2 flow at 323 K (a); and after 10 min in a N_2-free flow of CO/Ar at 323 K (b). The insert shows the correlation between the integrated intensities of the N_2-stretching at 2231 and the CO-stretching at 2061 cm^{-1} ($N = 24$, $R^2 = 0.947$, slope = 5.8 ± 0.1).

converts with CO slowly into the mer-tri-carbonyl. The correspondence to the mer-tri-carbonyl and the weak carbonyl band at 2129 together with the strong one at 2061 cm^{-1} let us propose the formation of a *trans*-dicarbonyl mono-dinitrogen complex of Ru, [Ru^{II}-

$(CO)_2(N_2)]^{2+}$. To confirm this assignment, we performed a ligand exchange with ^{13}CO and $^{15}N_2$ and compared the wavenumbers with those obtained in a related force field calculation using different structure models. Only the proposed *trans*-dicarbonyl mono-dinitrogen complex is able to reproduce the observed wavenumbers. As discussed already for the mixed carbonyl dinitrogen complexes, also in that mixed dicarbonyl dinitrogen complex the carbonyl stretching modes are influenced by the $^{14}N_2 - ^{15}N_2$ exchange revealing the mutual influence of carbonyl and dinitrogen ligands. The experimental fact that from the two carbonyl stretching frequencies only the highest a_1-mode is changed from 2129 to 2123 cm^{-1}, when $^{14}N_2$ is substituted by $^{15}N_2$, is an additional proof to the assumed structure with two *trans*-standing CO ligands and one *cis*-oriented N_2 ligand. Different to the a_1-mode, the second carbonyl stretching b_2-mode does not have a contribution from the N_2-stretching or interaction constants and remains, consequently, at 2061 cm^{-1}.

A comparison of the CO- and N_2-stretching force constants to those of the mer-tricarbonyl and the bis-dinitrogen complexes shows again the higher π-acceptor ability of the carbonyl ligand: $k(CO)$ decreases and $k(N_2)$ increases in the mixed complex. To the best of our knowledge, there are no homogeneous analogs of the mixed Ru carbonyl dinitrogen complexes as found in this work with the stabilising zeolite matrix. As for the Rh dinitrogen complexes

Table 1
Dinitrogen- and carbonyl-stretching wavenumbers (cm^{-1}) of well- defined surface species

Species	Rh^I/DAY [15,16]	Rh/Al$_2$O$_3$ [17]	Ru^{II}/DAY
fac-M(CO)$_3$	2119 + 2083 (only at low temp. [27])		2152 + 2091 + 2086
mer-M(CO)$_3$			2154 + 2081 + 2049
M(CO)$_2$	2115 + 2050	2099 + 2028	2082 + 2016 (at 523 K)
			2076 + 2006 (at 323 K)
M(CO)	2090	2061	2036
M(N$_2$)(CO)	2250 + 2058	2234 + 2048	2218 + 2023 (at 523 K)
			2257 + 2039 (at 323 K)
M(N$_2$)$_2$	2243 + 2217	2188	2207 + 2173 (at 523 K)
M(CO)$_2$(N$_2$)			2231 + 2129 + 2061

immobilised on the same support, this underlines the unique properties of dealuminated zeolites to stabilise unusual metal complexes not found in the homogeneous chemistry.

In Table 1, the well-defined surface species of Rh and Ru on dealuminated Y zeolite are compared. Table 1 includes also results obtained recently by Wovchko and Yates [17] for Rh/Al_2O_3. It is interesting to note that the wavenumbers of the species found on Al_2O_3 are systematically shifted to lower values. We believe that the higher wavenumbers with DAY as support are the result of the higher electronegativity of the oxygen atoms in the vicinity of the isolated Al sites in the dealuminated Y zeolite.

From Table 1, it is evident that the surface chemistry of Ru is considerably richer than that of Rh. As the wavenumbers and force constants of the dinitrogen stretching bands, also the stability of the dinitrogen complexes indicates a stronger interaction of N_2 with Ru supported on dealuminated zeolites as compared with Rh. This means, at the same time, that the dinitrogen ligand is more activated in the surface complexes of Ru than in those of Rh. It should be noted, however, that the wavenumbers are still to high to expect an easy splitting of the N≡N bond [2–6]. Future work on the reactivity of these complexes should show, whether the activation of molecular nitrogen can be used for surface reactions.

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