

# Ship-in-bottle synthesis of anionic Rh carbonyls in faujasites

L. Brabec\*, J. Nováková

*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic*

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## Abstract

Direct carbonylation of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  ion exchanged in sodium and potassium faujasites yields carbonyls, the composition of which depends on the extent of dehydration before carbonylation, and on the carbonylation temperature. Polynuclear anionic Rh carbonyls are formed at 25–100°C, if the water amount is sufficient. Greenish color of the species created at 75–100°C in NaX, KX and KY points to the  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  complex; at 50°C a white carbonyl is formed in NaX which structure seems to differ from the green complex in CO configuration. The anionic character of this species also follows from the lower wavenumber of terminal CO ligands in X zeolites and in KY compared to polynuclear neutral Rh carbonyl formed in less basic NaY. Carbonylation at 70–100°C after dehydration or carbonylation at 160–200°C lead to the formation of  $[\text{Rh}(\text{CO})_2]^+$ . This carbonyl reacts to the polynuclear complexes at 25–100°C after readsorption of water vapors. Individual carbonyl types once formed can be interchanged by varying the temperature and water amount. In addition to the FTIR spectroscopy, UV/VIS measurements and mass spectrometric analysis of ammonia released during the thermal decomposition of carbonyls were also employed. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The family of rhodium carbonyls is extensive, covering complexes of various nuclearity and charge (in reviews of carbonyls [1–4]). These complexes have been prepared in solutions [5–17], anchored on solid carriers [18–25] and embedded in zeolites [26–45]. Formation of finely dispersed metallic rhodium clusters has been the main expected goal in the studies of decomposition of the supported Rh carbonyls. In addition, it appeared that the carbonyls themselves (probably with participation of metallic Rh) can catalyze some reactions like hydroformylation of propylene, e.g. [31] or reduction of  $\text{N}_2\text{O}$ , e.g. [16].

### 1.1. Neutral and cationic Rh carbonyls — $\text{Rh-CO}_{\text{ads}}$ , $\text{Rh}_4(\text{CO})_{12}$ , $\text{Rh}_6(\text{CO})_{16}$ and $[\text{Rh}(\text{CO})_2]^+$

CO adsorbed on pure metal gives  $\text{Rh-CO}_{\text{ads}}$  species [46], while acid–base properties of various media including supports modify character of the Rh–CO bonding; e.g.  $\text{Rh}_4(\text{CO})_{12}$  was synthesized in solution [1,2,6,12,13], on oxides [25,32], and its presence on NaY was also reported [26,29,32,41].  $\text{Rh}_6(\text{CO})_{16}$  belongs to one of the most widespread complexes. It was prepared in solution [1,2,5,6,11,29,32], and also impregnated or synthesized on solids including zeolites [3,18–22,24–26,28,29,32–36,39–41,43,45]. The structure of Rh skeleton is octahedral, the CO arrangement is given by the formula  $\text{Rh}_6(\text{CO})_{12}(\mu_3\text{-CO})_4$  [1,2,5]. Rao et al. [36] found two temperature dependent bands of bridged CO ligands in NaY and assigned them to  $(\mu_2\text{-CO})$  and  $(\mu_3\text{-CO})$ .

\* Corresponding author.

$[\text{Rh}(\text{CO})_2]^+$  has also been very frequently reported [22,24,27–30,32–36,39–41,43,44], in NaY zeolites with one or both CO ligands bonded to the framework oxygens; in the former case the second CO is bonded to zeolitic water [30,39].

### 1.2. Anionic Rh carbonyls — $\text{Rh}_{(1-12)}\text{CO}_{(4-30)}$

Anionic Rh carbonyls with one to four negative charges were first synthesized in solutions. Some of them were prepared on  $\text{MgO}$  or  $\text{Al}_2\text{O}_3$  [20,21–23]. The anionic complexes can be intensively colored (refs. in Table 1).

Although the presence of neutral and cationic carbonyls in zeolites is well known, the formation of anionic Rh carbonyls has been only mentioned in NaY [37,38]; their existence was judged from the IR spectra of bridge bonded CO. The authors introduced rhodium into the zeolitic pores in the form of  $\text{Rh}(\text{CO})_2(\text{acac})$  and assumed that polynuclear Rh complexes are created, probably negatively charged due to the alkali nature of the sample (NaY treated with  $\text{NaN}_3$ ). Color of the complex was found as light yellow. Carbonylation of Rh chloropentammine complex in NaX zeolite was reported in [29], however, high CO pressures were employed (2–10 atm), and except  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{Rh}(\text{CO})_2^+$  an undefined mixture of carbonyls was obtained.

Because the ship-in-bottle synthesis of  $[\text{Pt}_3(\text{CO})_6]_2^{2-}$  [3,47,48] and neutral Pd carbonyls [49] from metal ammine cations in zeolites was successful, we have tried to prepare the Rh anionic carbonyl complexes by this method in alkali faujasites. Most attention was paid to Rh carbonyls in NaX, the assignment of the CO IR bands to different carbonyls was supported using zeolites with various basicity ( $\text{KX} > \text{NaX} \cong \text{KY} > \text{NaY}$ ). Processes of the carbonylation and the characterization of carbonyl complexes formed were examined in situ by FTIR and UV/VIS spectroscopies, and by the analysis of ammonia released during the thermal decomposition of Rh complexes.

## 2. Experimental

### 2.1. Zeolites

NaX (Si/Al = 1.25) was supplied by Serva International, Heidelberg, NaY (Si/Al = 2.5) by VU-

RUP, Slovak Republic. In some experiments, potassium forms of both zeolites were employed (ion exchange of Na for K using  $3 \times 0.5 \text{ M}$  solution of  $\text{KNO}_3$  at  $60^\circ\text{C}$  for 2 h). The alkali cations were partially ion exchanged for  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (Aldrich) at room temperature for 48 h to get 3 wt.% of Rh.

### 2.2. Carbonylation procedure

The samples were evacuated in situ before measurements usually at  $25^\circ\text{C}$  for 1 min (only to remove the air, samples were denoted as hydrated). Different pretreatments, if used, will be explicitly specified. 500 mbar (FTIR) or 1200 mbar (UV/VIS) of CO (Linde, 99.99) were allowed to react with the Rh chloropentammine complex at 25, 50, 75, 90, 100 and  $120\text{--}190^\circ\text{C}$ .

IR spectra were measured in situ during carbonylation using a Nicolet Protégé 460 FTIR spectrometer with a DTGS detector (resolution  $4 \text{ cm}^{-1}$ ). Weight of the zeolite wafers was  $7\text{--}8 \text{ mg cm}^{-2}$ .

UV/VIS spectra were recorded on small pellets (Ca 30 mg) using a Cary 4 spectrometer equipped with a Harrick reaction chamber; some measurements were carried out on powdered samples using a Perkin-Elmer Lambda 19 instrument.

The carbonyls formed were further treated in CO atmosphere at various temperatures, or decomposed by temperature-programmed heating (temperature-programmed decomposition —TPD) in vacuum with mass spectrometric detection of the gases evolved. TPD was measured using 5 mg of the zeolite. The gases released were led directly into the vacuum system of a Balzers QMG 400 quadrupole. Heating rate was  $5^\circ\text{C min}^{-1}$ , ion  $m/z = 16$  was used to represent the evolved ammonia.

## 3. Results

FTIR spectra of Rh carbonyl complexes formed in NaX after mild dehydration are shown in Fig. 1. Spectrum 1 (dashed) represents the parent  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  complex with characteristic  $\delta(\text{N-H})$  vibration at  $1340 \text{ cm}^{-1}$ . The carbonylation at  $50^\circ\text{C}$  for 48 h (spectrum 2) leads to a substantial decrease of this band; the band of  $\text{NH}_4^+$  at  $1460 \text{ cm}^{-1}$  appears instead, together with linearly bonded CO (strong band at 2022,

Table 1  
IR wavenumbers of CO bonds in cationic, neutral and anionic Rh carbonyls — literature data<sup>a</sup>

Complex	Wavenumber (cm <sup>-1</sup> )				Color	References
	On-top		Bridge			
[Rh(CO) <sub>2</sub> ] <sup>+</sup> (in zeolites)	Rh-CO-2O <sub>z</sub> Sym 2095–2100 As 2015–2024	Rh-CO-O <sub>z</sub> , H <sub>2</sub> O 2111–2115 2044–2050			–	[22,27–30,32–36,39–41,43,44]
[Rh(CO) <sub>2</sub> ] <sup>+</sup> (on oxide)	2085–2101	2004–2038			–	[22,24,27]
Rh(1 1 1)-CO	2016 (2065, higher exposure)		1835 (1855, higher exposure)		–	[46]
Rh <sub>2</sub> (CO) <sub>8</sub>	2087, 2062		1852, 1832		–	[29]
Rh <sub>4</sub> (CO) <sub>12</sub>	2064–2090		1830–1855		Red	[1,2,6,12,25,26,29,32,41]
Rh <sub>6</sub> (CO) <sub>16</sub> (in zeolites)	Sym 2092–2098	As 2064–2068	(μ <sub>3</sub> -CO) <sub>4</sub> 1760–1768	(μ <sub>2</sub> -CO) <sub>4</sub> 1800–1830	Rose, pale grey, yellow	[3,26,28,29,32–36,39–41,43,45]
Rh <sub>6</sub> (CO) <sub>16</sub> (on oxide or in solution)	2081–2077	2066	1795	1800–1805	Reddish	[1,2,5,6,11,16,18,19,21,22,24,25,29,32]
[Rh(CO) <sub>4</sub> ] <sup>-</sup>	1889–1900		–		Colorless	[2,12,13,16]
[Rh <sub>4</sub> (CO) <sub>11</sub> ] <sup>2-</sup>	1925–1975			1810–1813	Orange-red	[2,12,15,16]
[Rh <sub>5</sub> (CO) <sub>15</sub> ] <sup>-</sup>	2045–6, 2010–4		1785–8	1838–71	Red-brown, red-orange	[13,23]
[Rh <sub>6</sub> (CO) <sub>14</sub> ] <sup>4-</sup>	1985, 1945	1650	1700–1735	1890–1899	Dark red	[2,15]
[Rh <sub>6</sub> (CO) <sub>15</sub> ] <sup>2-</sup> (on oxide)	1968–2055		1757–1795	1802–1815	Green	[20]
[Rh <sub>6</sub> (CO) <sub>15</sub> ] <sup>2-</sup> (in solution)	2045–2060		1760–1790	1960–1990	Green	[2,9,10,11,20,21]
[Rh <sub>x</sub> (CO) <sub>y</sub> ] <sup>n-</sup>	1980		1766	1832	Light yellow	[37,38]
[Rh <sub>7</sub> (CO) <sub>16</sub> ] <sup>3-</sup>	1945–1987		1770–1775	1820	Dark green	[2,8,9,10,11,21]
[Rh <sub>9</sub> (CO) <sub>19</sub> ] <sup>3-</sup>	1957–1990		1770–1790	1822	Brown	[14]
[Rh <sub>12</sub> (CO) <sub>30</sub> ] <sup>2-</sup>	2000–2070		1770–1785	1807–1865	Violet	[1,2,7,11,23]
[Rh <sub>12</sub> (CO) <sub>34</sub> ] <sup>2-</sup>	2000–2050		1785	1835–1865	–	[10]

<sup>a</sup> Weak bands are not included; in [1,2,29,32] tables with literature data.

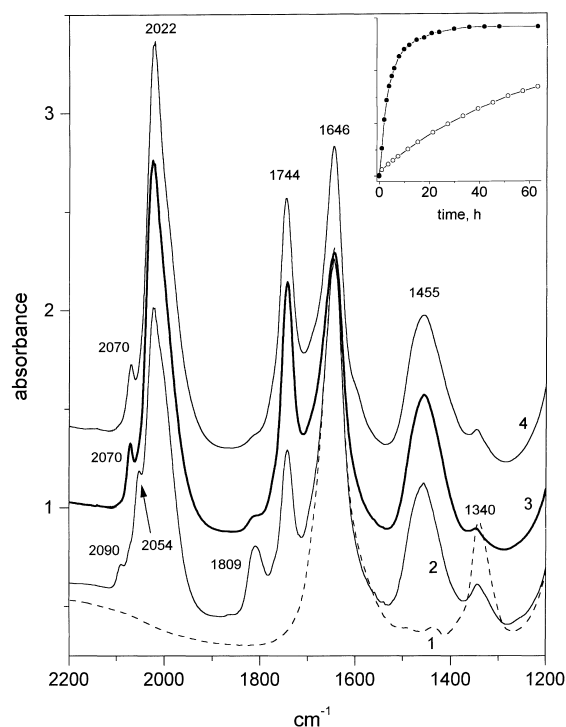


Fig. 1. Carbonylation of hydrated  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{NaX}$ , FTIR spectra. Spectra (always a new sample used): (1) dashed — the parent ammine (common for all samples). Carbonylated: at  $50^\circ\text{C}$  for 48 h — (2) solid fine; at  $75^\circ\text{C}$  for 48 h — (3) solid bold; at  $100^\circ\text{C}$  for 15 h — (4) solid fine. Inset: effect of dehydration on the carbonylation rate — integrated intensities of on-top bonded CO vs. time; solid circles — hydrated sample, open circles — dehydrated sample (evacuated at  $60^\circ\text{C}$  for 5 min).

shoulders at  $2090$  and  $2054\text{ cm}^{-1}$ ) and bridge-bonded CO at  $1809$  and  $1744\text{ cm}^{-1}$ . The band at  $1646\text{ cm}^{-1}$  belongs to deformation vibrations of water. Color of the sample remains white. When the carbonylation is carried out at  $75^\circ\text{C}$  for 24–48 h, the sample becomes green and its spectrum is slightly changed (spectrum 3). The position of the dominant band of the on-top bonded CO is the same, the two previous shoulders disappear and a new one at  $2070\text{ cm}^{-1}$  is formed. The intensity of the bridge-bonded CO at  $1809\text{ cm}^{-1}$  decreases, that at  $1744\text{ cm}^{-1}$  increases. Practically the same spectrum appears after carbonylation at  $100^\circ\text{C}$  (spectrum 4), and survives even the heating to  $130^\circ\text{C}$  (not shown). Only the band at  $1809\text{ cm}^{-1}$  disappears and the sample slowly loses its green color.

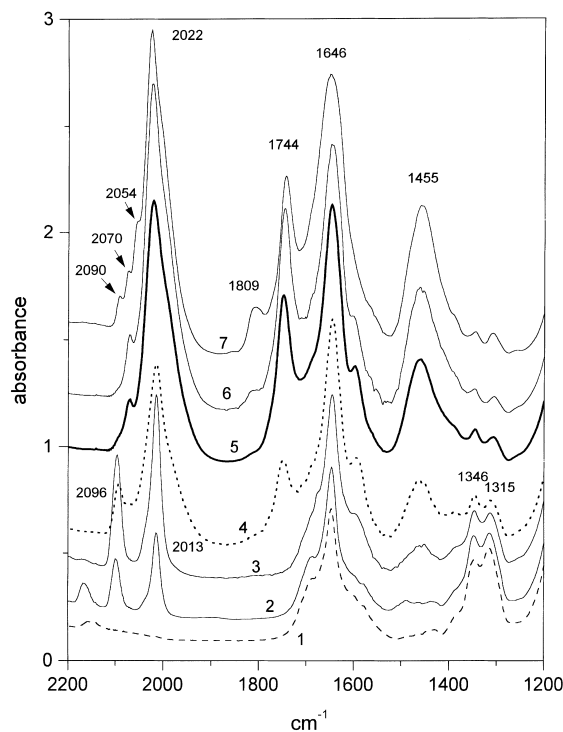


Fig. 2. Carbonylation of more dehydrated  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{NaX}$ , FTIR spectra. Spectra (one sample used): (1) dashed — the parent ammine dehydrated at  $25^\circ\text{C}$  for 15 h. Carbonylated: at  $70^\circ\text{C}$  for 3 h — (2) solid fine; at  $90^\circ\text{C}$  for 12 h — (3) solid fine; at  $90^\circ\text{C}$  for 37 h — (4) dotted; at  $90^\circ\text{C}$  for 86 h — (5) solid bold;  $70^\circ\text{C}$  for 36 h — (6) solid fine;  $25^\circ\text{C}$  for 60 h — (7) solid fine.

The inset in Fig. 1 shows strong effect of the zeolite dehydration on the carbonylation rate. The time dependency of the integrated bands of on-top bonded CO formed at  $75^\circ\text{C}$  after 1 min evacuation at  $25^\circ\text{C}$  and after 5 min evacuation at  $60^\circ\text{C}$  is displayed. In the latter case, the water amount is 1.5–2 times lower, while the extent of carbonylation during first 10 min is five to six times lower.  $[\text{Rh}(\text{CO})_2]^+$  was not registered at this level of dehydration (cf. Fig. 2).

Fig. 2 displays the IR spectra after long dehydration (15 h) at  $25^\circ\text{C}$  prior to carbonylation: the N–H band of parent amines (spectrum 1, dashed) is splitted into two bands vibrating at  $1346$  and  $1315\text{ cm}^{-1}$ ; the intensity of the band belonging to water (at  $1646\text{ cm}^{-1}$ ) is of about three times lower than that in Fig. 1. The carbonylation at  $70^\circ\text{C}$  for 3 h leads to the  $[\text{Rh}(\text{CO})_2]^+$  complex with two linearly bonded CO — at  $2096$  and

2016  $\text{cm}^{-1}$  (spectrum 2). When this sample is heated at 90°C for 12 h (spectrum 3), the extent of carbonylation is higher: the bands of the parent amines partially decrease.

Prolongation of the carbonylation at 90°C to 37 h changes the character of CO bonding (spectrum 4, dotted): the intensity of the band at 2096  $\text{cm}^{-1}$  decreases and a bridge-bonded CO at 1746  $\text{cm}^{-1}$  is formed; simultaneously, the intensity of the  $\text{NH}_4^+$  band at 1455  $\text{cm}^{-1}$  increases. Further prolongation of carbonylation at 90°C ( $\Sigma 86$  h) results in spectrum 5 (bold) which is very similar to spectrum 4 in Fig. 1. When the sample was then cooled to 70°C and held at this temperature for 36 h (spectrum 6), CO bands strongly resemble those of the green carbonyl as shown in Fig. 1 by spectrum 3. Temperature decrease to 25°C for 60 h (spectrum 7) results in CO bands with shoulders at 2090 and 2054  $\text{cm}^{-1}$  which belong to the white carbonyl (cf. spectrum 2 in Fig. 1).

When the hydrated sample is directly carbonylated at relatively high temperature of 180°C for 1 h,  $[\text{Rh}(\text{CO})_2]^+$  is formed (Fig. 3, spectrum 2, inset). The band of  $\text{NH}_4^+$  is formed on the account of the band of  $\text{NH}_3$  ligands, and the band belonging to water decreases due to the increased temperature (cf. spectrum 1, dashed). When the sample is cooled to 25°C, water is readsorbed, and character of the Rh complexes is changed: some rests of  $[\text{Rh}(\text{CO})_2]^+$  remain, but a polynuclear complex is formed. A new band at 1840  $\text{cm}^{-1}$  is formed, the band at 1810  $\text{cm}^{-1}$  is higher than that at 1744  $\text{cm}^{-1}$  (cf. Fig. 1, spectrum 2 and spectrum 3 in this figure). The shoulders at 2090 and 2054  $\text{cm}^{-1}$  belonging to the on-top bonded CO band are characteristic for the white complex formed at 50°C. Longer stay at 25°C for 5 h (spectrum 4) and 37 h (spectrum 5, bold) removes partially the band at 1810  $\text{cm}^{-1}$  and the ratio of the band at 1810 to that at 1744  $\text{cm}^{-1}$  decreases.

Carbonylation of Rh chloropentammine in KX leads to the same carbonyls as are those in NaX; however, the reaction rate is substantially higher — the carbonylation at 75°C in KX is complete in 20 h, while only half of the parent Rh complex is carbonylated in NaX. Carbonylation in NaY almost does not proceed at this temperature. Hydrated NaY with the same amount of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  as that in Na- and KX exhibits spectra shown in Fig. 4, upper part: a strong narrow band of on-top bonded

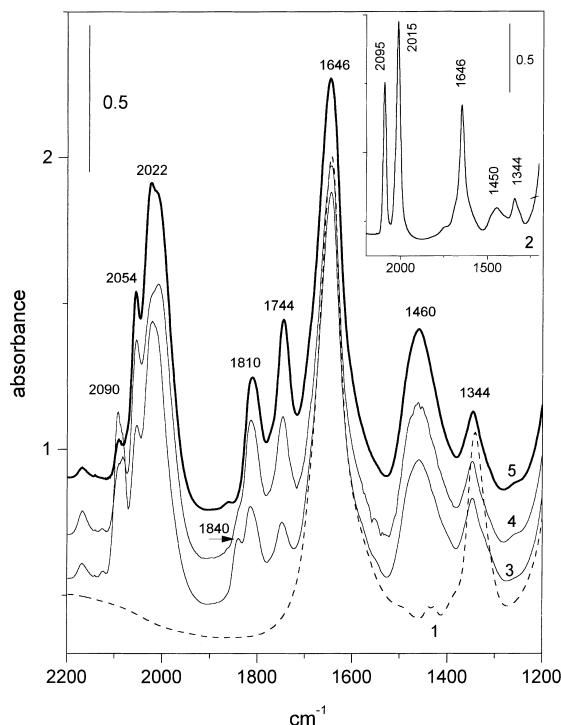


Fig. 3. Carbonylation of hydrated  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]/\text{NaX}$ , effect of higher carbonylation temperature, FTIR spectra. Spectra (one sample used): (1) dashed — the parent ammine. Carbonylation: at 180°C for 1 h — (2, inset); at 25°C for 1 h — (3) solid fine; for 5 h — (4) solid fine; for 37 h — (5) solid bold.

CO occurs at 2098  $\text{cm}^{-1}$ , the bridge bonded CO vibrate at 1770  $\text{cm}^{-1}$ . Heating at 180°C does not change the spectrum, only after evacuation at this temperature the typical bands of  $[\text{Rh}(\text{CO})_2]^+$  splitted to 2098–2108 and 2022–2042  $\text{cm}^{-1}$  appear (not shown in the figure). Carbonylation of KY is shown in the bottom part of Fig. 4: the dominant on-top bonded CO occurs at substantially lower wavenumber (2000–2020  $\text{cm}^{-1}$ ). Intermediate appearance of the band at 2094  $\text{cm}^{-1}$  could belong to cationic or neutral Rh carbonyl. The bridge-bonded CO vibrate at 1778 and 1748  $\text{cm}^{-1}$ . Heating to 180°C results in the formation of  $[\text{Rh}(\text{CO})_2]^+$  with bands at 2091 and 2018  $\text{cm}^{-1}$  (not shown).

UV/VIS spectra are given in Fig. 5 for  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  carbonylated at 75°C after mild and stronger dehydration of the sample: dashed spectrum corresponds with the green carbonyl, solid spectrum with the Rh

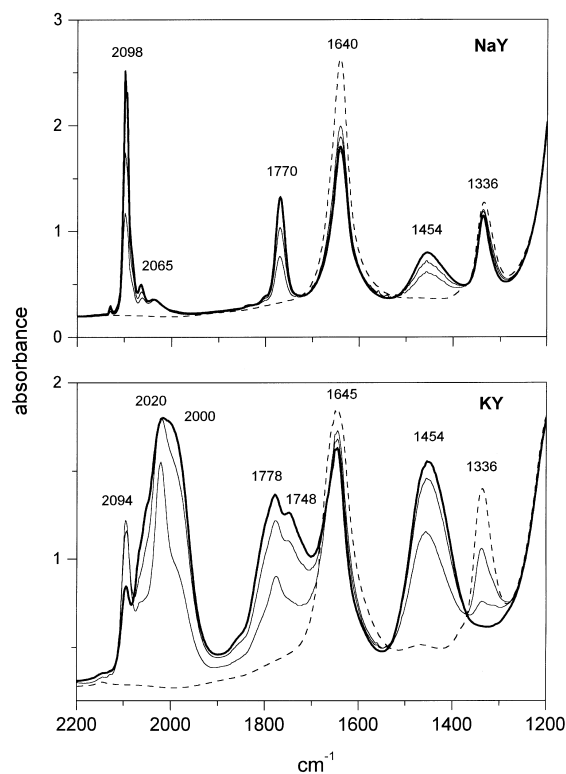


Fig. 4. Carbonylation of hydrated  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{NaY}$  and  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{KY}$ , FTIR spectra. Spectra: dashed — the parent ammine in NaY and KY; solid fine — carbonylation at  $100^\circ\text{C}$  for 4 and 8 h; solid bold — for 20 h.

dicarbonyl cation. The latter spectrum exhibits two well resolved bands at 260 and 320 nm; these bands are not well resolved in the sample containing more water, but, in addition to these two bands, the sample exhibits a broad weak band centered at 600 nm. This band was repeatedly found in the spectra of the green carbonyls. The effect of dehydration on the resolution of the former two bands is displayed in the inset of Fig. 5, showing UV/VIS spectra of  $[\text{Rh}(\text{NH}_3)_6]^{3+}$  carbonylated to  $[\text{Rh}(\text{CO})_2]^+$ .

TPD curves of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  and Rh carbonyls embedded in NaX are given in Fig. 6. The release of ammonia is the highest from the Rh ammine and occurs in several maxima between 100 and  $400^\circ\text{C}$ . The green Rh anionic carbonyl releases a little lower amount of ammonia, and virtually one maximum occurs at about  $220^\circ\text{C}$ . The amount of ammonia evolved from the Rh dicarbonyl is relatively very low and

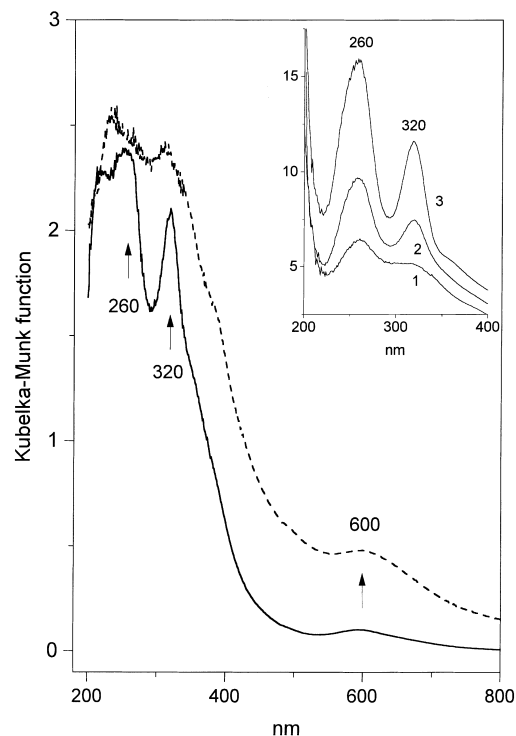


Fig. 5. Carbonylation of hydrated and dehydrated  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{NaX}$ , UV/VIS spectra. Spectra: solid — dehydration at  $120^\circ\text{C}$  for 2 h; dashed — dehydration at  $25^\circ\text{C}$  for 15 min; carbonylation for 48 h. Inset: variously dehydrated  $[\text{Rh}(\text{NH}_3)_6]/\text{NaX}$ ; spectra 1, 2, 3 — carbonylation at  $180^\circ\text{C}$  for 3 h after dehydration (for 5 min) at 60, 120 and  $180^\circ\text{C}$ , respectively.

is shifted to the lowest temperature. Integrated TPD curves for the parent ammine, green carbonyl and cationic Rh dicarbonyl correspond to the following values (in arbitrary units): 7.4, 5.9 and 2.3, respectively.

## 4. Discussion

### 4.1. The charge and structure of Rh complexes

The CO bands at  $2096$  and  $2016\text{ cm}^{-1}$  (Figs. 1–3) can be unambiguously assigned to the  $[\text{Rh}(\text{CO})_2]^+$  cationic complex. These wavenumbers are, in agreement with literature assigned to symmetric and asymmetric CO vibrations, respectively (cf. Table 1

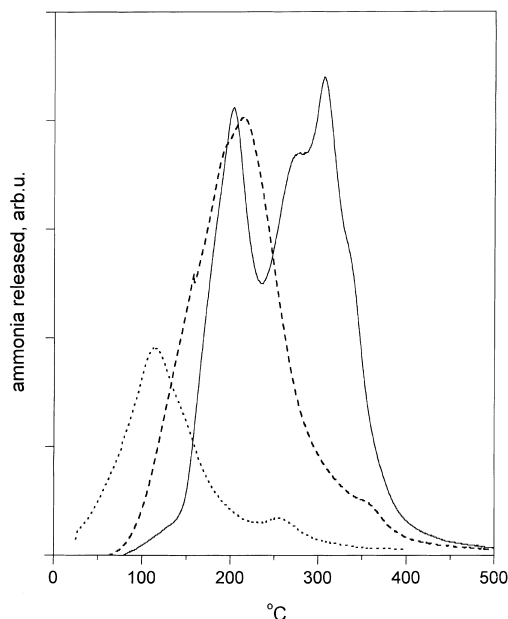


Fig. 6. TPD of  $[\text{Rh}(\text{NH}_3)_5(\text{Cl})]/\text{NaX}$  before and after carbonylation. Curves: solid — parent ammine; dashed — hydrated sample carbonylated at  $70^\circ\text{C}$  for 48 h; dotted — dehydrated sample carbonylated at  $180^\circ\text{C}$ .

with Table 2 containing experimental data). Splitting of the bands caused by the bonding to only zeolitic oxygens and to zeolitic oxygens and water

ligands [30,39,40] is not visible in  $\text{RhNaX}$  contrary to  $\text{RhNaY}$  after vacuum heating to  $200^\circ\text{C}$  (Table 2). The agglomeration of the cationic  $[\text{Rh}(\text{CO})_2]^+$  dicarbonyl to polynuclear Rh carbonyl complexes as well as the reverse reaction have been often reported (e.g. [21,24,33,36,39,43]). Usually, the formation of polynuclear neutral  $[\text{Rh}_6(\text{CO})_{16}]$  complex is suggested, in NaY with characteristic on-top bonded CO at  $2098\text{ cm}^{-1}$ , and bridge-bonded CO at  $1760\text{ cm}^{-1}$  ( $\mu_3\text{-CO}$ ) and at  $1830\text{ cm}^{-1}$  ( $\mu_2\text{-CO}$ ). The relative extinction coefficient equal to 0.53 was estimated for the on-top bonded CO from the absorbance ratio to the bridge bonded CO (1.6), considering 12 linearly bonded CO and four bridge-bonded CO [36]. We have found almost the same wavenumbers in carbonylated Rh chloropentamine dications in NaY, however, in NaX the on-top bonded CO is shifted by  $76\text{ cm}^{-1}$  to lower wavenumber ( $2022\text{ cm}^{-1}$ , see Figs. 1–3). Our experimental ratios of absorbances of on-top and bridge-bonded CO are 2.3 in NaY and 1.3–1.6 in NaX. Our lower values in NaX could correspond with the higher amount of bridging CO ligands in anionic carbonyls (for  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  according to [50] the ratio should be  $9/6 = 1.5$ ), however, the theoretical calculations of the effect of carbonyl charge and composition on the intensities of CO IR bands are missing. Carbonylation of Rh chloropentamine in KX yields practically the same CO vibrations

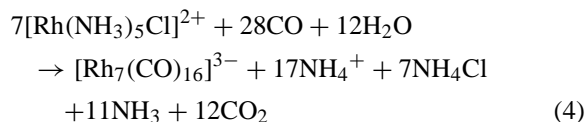
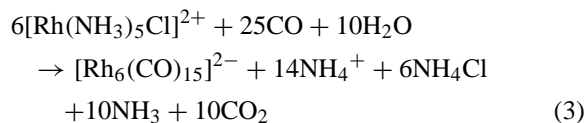
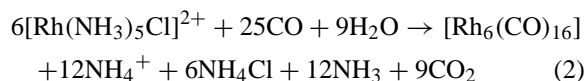
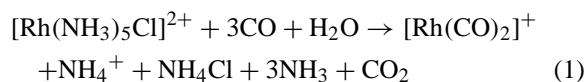
Table 2  
IR CO wavenumbers of Rh carbonyls embedded in faujasites (this work)<sup>a</sup>

Zeolite	Pretreatment	<i>T</i> of carbonyls ( $^\circ\text{C}$ )	Wavenumbers <sup>a</sup> ( $\text{cm}^{-1}$ )	Assignment
NaX	Hydrated	50	2090 w, 2054 w, 2022 s, 1809 m, 1744 ms	$[\text{Rh}_6(\text{CO})_9(\mu_2, \mu_3\text{-CO})_6]^{2-}$
	Hydrated	75 or 100	2070 w, 2022 s, 1809 vw, 1744 s	$[\text{Rh}_6(\text{CO})_9(\mu_3\text{-CO})_6]^{2-}$
	Hydrated	180	2095 s, 2015 s	$[\text{Rh}(\text{CO})_2]^+$
	Dehydrated	Cooled to 25	2090 w, 2054 m, 2022 s, 1810 ms, 1744 ms	$[\text{Rh}_6(\text{CO})_9(\mu_2, \mu_3\text{-CO})_6]^{2-}$
		90	2096 s, 2013 s	$[\text{Rh}(\text{CO})_2]^+$
	Cooled to 70	2070 w, 2022 s, 1809 vw, 1744 s	$[\text{Rh}_6(\text{CO})_9(\mu_3\text{-CO})_6]^{2-}$	
KX	Hydrated	75	2070 w, 2020 s, 1975 sh, 1935 sh, 1747 ms	$[\text{Rh}_6(\text{CO})_9(\mu_3\text{-CO})_6]^{2-}$
NaY	Hydrated	100 or 130	2098 vs, 2065 w, 2038 vw, 1770 s	$\text{Rh}_6(\text{CO})_{12}(\mu_3\text{-CO})_4$
		180, evacuated	2108 m–2098 sh, 2042–2022 m	$[\text{Rh}(\text{CO})_2]^+$
	Hydrated	180	2105 s, 2036 s	$[\text{Rh}(\text{CO})_2]^+$
		Cooled to 25	2098 s, 2055 w, 2031 s, 1836 m, 1770 w	$\text{Rh}_6(\text{CO})_{12}(\mu_2\text{-CO})_4$ or $\text{Rh}_4(\text{CO})_{12}$
	Heated to 100	2098 vs, 2065 w, 1770 s	$\text{Rh}_6(\text{CO})_{12}(\mu_3\text{-CO})_4$	
KY	Hydrated	75	2094 m, 2054 m, 2016 s, 1813 sh, 1780 m	$[\text{Rh}_6(\text{CO})_{15}]^{2-}$ + small fraction of neutral $\text{Rh}_6$ or $\text{Rh}_4$ carbonyl
		100	2094 m, 2054 sh, 2020–2000 s, 1778 s, 1748 m	
	Heated to 180	2091 vs, 2018 vs	$[\text{Rh}(\text{CO})_2]^+$	

<sup>a</sup> Intensities: vs — very strong; s — strong; ms — medium strong; m — medium; w — weak; vw — very weak; sh — shoulder.

(Table 1); these wavenumbers also predominate in RhKY, while in NaY occur at the same wavenumber as that found in [36]. Chini in [1] suggests a linear decrease of wavenumbers with increasing negative charge of the complex related to the number of metal atoms. Shift of the position of on-top bonded CO (2098 → 2022 cm<sup>-1</sup>) in our Rh complexes from less basic NaY to KY, KX and NaX of higher basicity (the dependence of zeolitic oxygen basicity on the nature of alkali ions and Si/Al ratio, e.g. in [51]) is thus in line with the assumption of the formation of neutral polynuclear Rh carbonyl in NaY, prevailing anionic carbonyl in KY and virtually only anionic carbonyl in NaX and KX. The neutral polynuclear carbonyl can be either Rh<sub>6</sub>(CO)<sub>16</sub> (at ≅100°C) or Rh<sub>4</sub>(CO)<sub>12</sub> (at calculated room temperature) [41].

If the NH<sub>4</sub><sup>+</sup> ions accompanying the formation of cationic [Rh(CO)<sub>2</sub>]<sup>+</sup> and neutral or dianionic hexanuclear (trianionic heptanuclear?) Rh carbonyls are formed according to the Eq. (1)–(4):



then, NH<sub>4</sub><sup>+</sup>/Rh ratios are 2, 3, 3.3 and 3.4 for [Rh(CO)<sub>2</sub>]<sup>+</sup>, Rh<sub>6</sub>(CO)<sub>16</sub>, [Rh<sub>6</sub>(CO)<sub>15</sub>]<sup>2-</sup> and [Rh<sub>7</sub>(CO)<sub>16</sub>]<sup>3-</sup>, respectively. The last three values are too close, so that they cannot be used to determine the charge of the polynuclear carbonyl. This holds for both IR spectra and TPD of ammonia. The formation of a polynuclear Rh carbonyl can be at least deduced.

Green color of the anionic Rh carbonyl, which supports our assignment of the polynuclear species to [Rh<sub>6</sub>(CO)<sub>15</sub>]<sup>2-</sup>, was also reported for the [Rh-

(CO)<sub>16</sub>]<sup>3-</sup> trianion (Table 1). This species [Rh<sub>7</sub>(CO)<sub>7</sub>-(μ<sub>2</sub>-CO)<sub>6</sub>(μ<sub>3</sub>-CO)<sub>3</sub>]<sup>3-</sup> [8] also cannot be excluded, however, its ratio of linearly to bridge-bonded CO should be even lower than for the [Rh<sub>6</sub>(CO)<sub>15</sub>]<sup>2-</sup> complex (equal to 7/9 = 0.78).

As concerns the differences in the polynuclear carbonyls formed at 50, 75 and 90–100°C in NaX, they differ in: (i) weak shoulders accompanying the dominant CO on-top bonded ligand at 2022 cm<sup>-1</sup> — either (2090 + 2054) cm<sup>-1</sup> at 50°C, or 2070 cm<sup>-1</sup> at 75–100°C, (ii) in the relative intensities of the bridge bonded CO at 1809 cm<sup>-1</sup> compared to that at 1744 cm<sup>-1</sup> (the former one strongly decreases with increasing temperature), and (iii) in color from white to green and only weakly green. The position of the dominant on-top bonded CO band remains the same, as well as the linear/bridge bonded CO ratio. It is therefore tempting to assume that these changes belong to the isomers of one species occurring in the bridge-bonded CO. The band at 1809 cm<sup>-1</sup> can reflect (μ<sub>2</sub>-CO) ligands, the band at 1744 cm<sup>-1</sup> may belong to (μ<sub>3</sub>-CO) ligands. Similar assignment was done by Rao et al. [36] for the neutral hexanuclear Rh carbonyl in NaY. The conversion of (μ<sub>2</sub>-CO) to (μ<sub>3</sub>-CO) by increasing temperature agrees with that reported in the latter reference. Both these bridge bonded CO ligands were also found by Takahashi et al. [33,34], however, they were assigned to the formation of polynuclear Rh carbonyls on the surface or in near-surface supercages of NaY zeolite.

The carbonylation of Rh<sup>3+</sup> cations in zeolites (NaY) has been assumed to proceed via the reduction of primarily formed [Rh(CO)<sub>2</sub>]<sup>+</sup> (e.g. [29,31,40]). This certainly occurs in our NaX when the zeolite is more strongly dehydrated before carbonylation (see Fig. 2), or even at room temperature from Rh<sup>3+</sup> without ammine ligands or after their partial removal (to be published).

It should be mentioned that some Cl<sup>-</sup> ligands probably stayed in the zeolites from the Rh chloropentammine cations used as the source of Rh (majority of them should be removed by hydrolysis during the preparation [30]). If the [Rh(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> was used instead of [Rh(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> in NaX, the carbonylation did not begin even at 100°C in hydrated sample. [Rh(CO)<sub>2</sub>]<sup>+</sup> was formed after dehydration, and polynuclear carbonyls were created from this Rh carbonyl cation after water addition. The substantially



easier carbonylation of the samples with some chlorine remainders points to a favourite role of chlorine ions.

#### 4.2. UV/VIS spectra

The UV/VIS spectra of our Rh carbonyls exhibit virtually the same bands at 260 and 320 nm (better resolved in dehydrated samples); these bands were also reported in [17]. The authors found for  $\text{Rh}(\text{Cl})(\text{CO})_2$  in various matrices at  $-261^\circ\text{C}$  two bands at 258–265 and 315–326 nm, which are identical with our bands in Fig. 4. In addition, we have found a band at 600 nm assigned exclusively to the green anionic complex. Authors of [16] identified two Rh anionic complexes by UV/VIS spectra:  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$  with a weak band at 346 nm and  $[\text{Rh}(\text{CO})_4]^-$  with a strong band at 265 nm. These isolated data are not consistent with ours.

#### 5. Conclusions

$[\text{Rh}(\text{CO})_2]^+$  and polynuclear Rh carbonyl complex were prepared by ship-in-bottle carbonylation of Rh chloro-pentammine cations in faujasites.

1. The polynuclear carbonyls in basic NaX, KX and KY were assigned to  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  due to lower wavenumber of the on-top bonded CO compared to the wavenumber of Rh carbonyl in less basic NaY, where the formation of the neutral  $[\text{Rh}_6(\text{CO})_{16}]$  is assumed.
2. Configuration of bridged CO ligands in  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  changes in dependence on the carbonylation temperature in the range of 25–100°C. The green isomer exhibits in UV/VIS spectrum a characteristic band centered at 600 nm.
3. Higher carbonylation temperature as well as higher zeolite dehydration prior to carbonylation lead to the primary formation of the  $[\text{Rh}(\text{CO})_2]^+$ ; this complex can be changed to polynuclear carbonyls at lower temperature and in the presence of water. These changes proceed reversibly.

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