# REDOX CHEMISTRY OF HIGHLY DISPERSED RHODIUM IN ZEOLITE NaY

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NaY zeolite exchanged with $[Rh(NH_3)_5Cl]^{2+}$ ions have been studied using temperature programmed oxidation (TPO), temperature programmed reduction (TPR), and Fourier transformed infrared spectroscopy. The TPO profiles show that ammine ligands in NaY encaged $[Rh(NH_3)_5Cl]^{2+}$ are destroyed above 300 °C, whereas the Rh precursor ion remains intact after calcination at 200 °C. TPR profiles in conjunction with the $CO_{ads}$ IR spectra show that the reducibility of Rh by $H_2$ is largely controlled by the concentration of the surface protons, i.e.

$$Rh^{3+} + H_2 \rightleftharpoons Rh^{+} + 2H^{+}$$

$$Rh^{+} + \tfrac{1}{2}H_2 \rightleftharpoons Rh^{0} + H^{+}$$

In the presence of ammonia, the protons are neutralized and $Rh^{3+}$ is reduced to $Rh^0$. However, reduction remains incomplete when the concentration of protons is high. The ammonia was provided either by $NH_3$ admission or by conservation of ammine ligands by controlled calcination. CO adsorption does not lead to reoxidation of $Rh^0$ particles to $Rh^+$ ions.

## 1. Introduction

Oxide supported rhodium is one of the most intriguing heterogeneous catalysts. Its propensity to catalyze hydrogenation, hydroformylation and other reactions, in particular the conversion of synthesis gas to methanol, higher oxygenates and hydrocarbons, has stimulated much research in recent years. Attention has been focused on the chemical interaction of supported Rh with oxide supports or other catalyst modifiers [1–14]. Of special interest is the formation of zeolite encaged carbonyl clusters of rhodium [15–20].

Some basic facts about the redox chemistry of highly dispersed rhodium on oxide supports are, however, still mystifying and need to be elucidated. Various authors have reported that, by reducing supported $Rh^{3+}$ with hydrogen, followed

by admission of carbon monoxide, a cationic monorhodium dicarbonyl, $Rh^+(CO)_2$, is formed [17–28]. This dicarbonyl is identified by IR bands at 2024, 2045, 2100 and 2113 $cm^{-1}$ [19,29]. It has been proposed [17,18,24–26] that $H_2$ first reduces the $Rh^{3+}$ to Rh metal; the oxidation of $Rh^0$ to $Rh^+(CO)_2$, in the presence of CO, is then attributed to Rh-Rh bond rupture by CO and a reaction of $Rh^0$ with surface hydroxyl groups, i.e. protons oxidize $Rh^0$ to $Rh^+$:

$$Rh^0 + H^+ \rightleftharpoons Rh^+ + \tfrac{1}{2}H_2. \quad (1)$$

This evolution of $H_2$ has, however, never been observed for supported rhodium. Also, it is unknown whether the CO serves merely as an IR active ligand that makes the cationic $Rh^+$ visible by FTIR spectroscopy, or whether it is instrumental in the hypothetical reoxidation of $Rh_x$ to $Rh^+$. One might even ask whether the Rh atom in $Rh^+(CO)_2$ ever passed through the stage of $Rh^0$ or whether reduction of supported $Rh^{3+}$ with $H_2$ stops at the stage of $Rh^+$:

$$Rh^{3+} + H_2 \rightleftharpoons Rh^+ + 2H^+. \quad (2)$$

It occurred to us that the subsequent reduction:

$$Rh^+ + \tfrac{1}{2}H_2 \rightleftharpoons Rh^0 + H^+ \quad (3)$$

which is, of course the reversal of (1), might be limited by a chemical equilibrium i.e. controlled by the concentration of acidic protons on the catalyst surface. Several authors have investigated the oxidation states of Rh [30–34]. Previous research has shown that in zeolite supported Pt, reoxidation of isolated $Pt^0$ atoms in the sodalite cages by protons occurs at temperatures between 400 and 500 °C [35]. In the case of zeolite supported Ni, it could also be shown that multiatomic particles are oxidized by zeolite protons [36].

In the present paper, we report on FTIR results of rhodium carbonyls encaged in NaY. Ammonia was applied by two methods to provide a thermodynamic sink for the protons formed in eq. (2) and eq. (3). The first method was conservation of some of the ammine ligands of the original Rh-ammine complex ion by controlled calcination. The second method was admission of ammonia to the reduced catalyst, followed by a second reduction. Temperature programmed reduction (TPR) was used to monitor the reducibility of the rhodium before and after binding zeolite protons to $NH_3$. After admission of carbon monoxide the FTIR spectra of the rhodium carbonyls and the carbonyl clusters were registered.

## 2. Experimental

### 2.1. CATALYST PREPARATION

Rh supported on NaY was prepared by ion-exchange of NaY (LZY-52, Linde). The exchange was performed by dropwise addition of a 0.001 M aqueous solution

of $[Rh(NH_3)_4Cl]Cl_2$ (Engelhard) to a dilute zeolite slurry in doubly deionized water (200 ml/g) at 70 °C for 24 hours. After the exchange, the catalyst was dried and calcined in pure $O_2$ at atmospheric pressure. The temperature ramp was programmed at 0.5 °C/min from 23 °C to a specified temperature ($T_C$) and held at this temperature for 2 hours. Atomic absorption analysis determined the catalyst to contain 1.57 wt% (or 4.41 wt%) Rh.

### 2.2. TEMPERATURE PROGRAMMED OXIDATION (TPO) AND REDUCTION (TPR)

The TPO and TPR data were obtained and analyzed by a procedure similar to that described by Homeyer and Sachtler [37]. TPO was performed on an uncalcined sample, 180 mg of 4.41 wt% Rh/NaY, in 5% $O_2$/He flow (60 ml/min), while ramping the temperature from 23 °C to 500 °C at a heating rate of 8 °C/min. TPR was performed on a sample, 120 mg of 4.41 wt% Rh/NaY, calcined to 500 °C. The sample was cooled to −80 °C in Ar and then Ar was replaced by a flowing (25 ml/min) mixture of $H_2$/Ar (5% $H_2$). The temperature was ramped from −80 °C to 250 °C at 8 °C/min. At this reduction temperature, the gas flow was returned to Ar and the sample was allowed to cool to room temperature to remove most of the adsorbed hydrogen. After reaching room temperature, ammonia gas was introduced at atmospheric pressure for 10 minutes and a subsequent TPR was performed.

### 2.3. INFRARED SPECTROSCOPY

IR spectra were recorded by a Nicolet 60SX single-beam Fourier Transform infrared spectrometer at a resolution of 1 $cm^{-1}$. In general, the samples were scanned 200 times to insure a good signal/noise ratio. Samples consisting of 40 mg of 1.57 wt% Rh/NaY were pressed into 20 mm diameter wafers; calcination was performed in pure $O_2$ at atmospheric pressure in the IR cell. The temperature ramp was programmed at 0.5 °C/min from 23 °C to a specified calcination temperature ($T_C$) and held at this temperature for 2 hours. Oxygen was then replaced by flowing Ar for 20 minutes at $T_C$ and the sample was allowed to cool to room temperature. Reduction was performed in a pure $H_2$ flow at atmospheric pressure. The temperature ramp was programmed at 8 °C/min from 23 °C to a specified reduction temperature ($T_R$) and held at this temperature for 20 minutes. When desired, $H_2$ flow at $T_R$ was replaced by the following sequence of flowing gases: (1) $NH_3$ for 5 min, (2) Ar for 5 min, (3) $H_2$ for 10 min, (4) $NH_3$ for 5 min, and (5) $H_2$ for 15 min. Hydrogen was then replaced by Ar for 20 minutes at $T_R$ and the sample was allowed to cool to room temperature.

Flowing CO was introduced at atmospheric pressure and at 23 °C for 10 minutes. After CO adsorption, the cell was purged with Ar at 23 °C and IR spectra were recorded. Background spectra were taken with a wafer which had

not been exposed to CO, in order to ratio the CO adsorption spectra with the background spectra.

In this paper, the notation Rh/NaY($T_C/T_R$) will be used, indicating the calcination and reduction temperatures (in °C) to which a Rh/NaY sample had been exposed. And the notation $Rh/NaY_{NH_3}(T_C/T_R)$ will be used to indicate neutralization of the sample.

## 3. Results and discussion

The TPO profiles shown in fig. 1 show that ammine ligands are oxidized to $N_2$ and $H_2$ at calcination temperatures above 300 °C, as reported previously by Primet et al. [20].

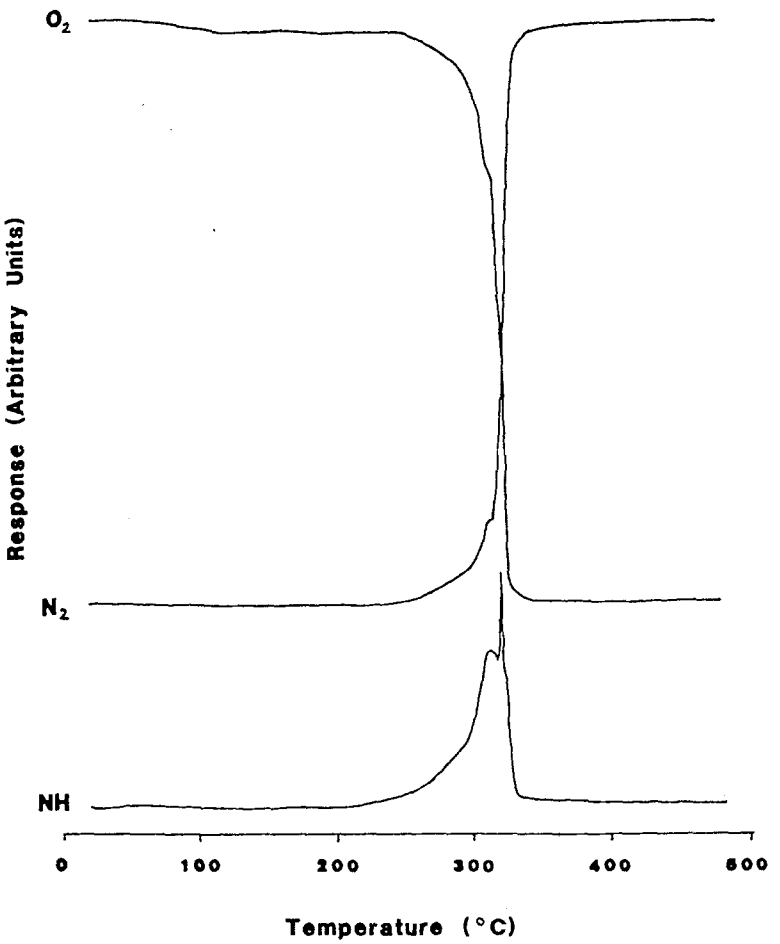


Fig. 1. TPO of $[Rh(NH_3)_5Cl]^{2+}$/NaY; masses 15(NH), 28($N_2$) and 32($O_2$) are plotted versus temperature.

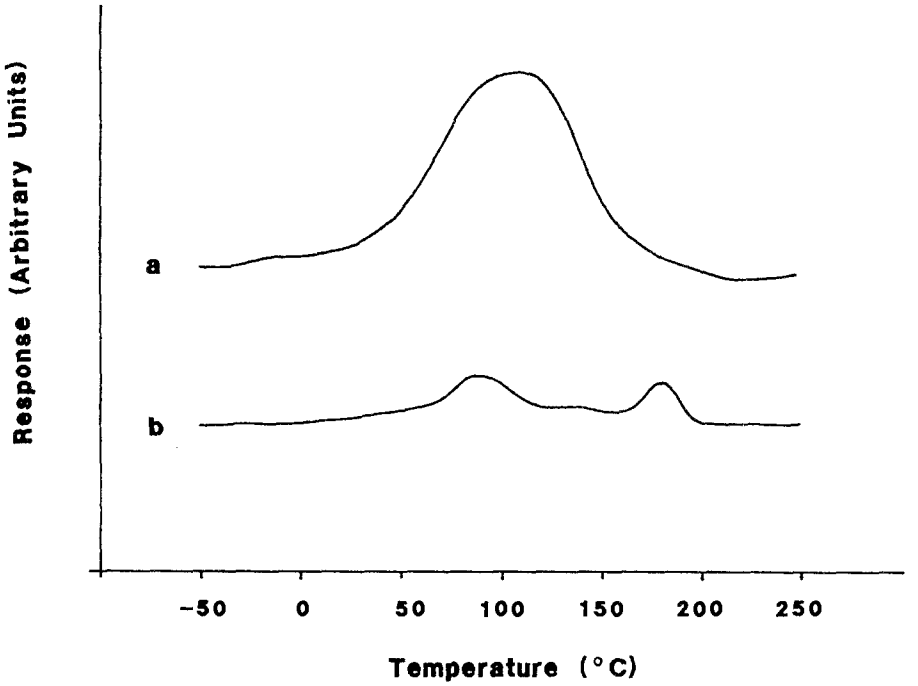


Fig. 2. (a) TPR of $Rh^{3+}$/NaY sample calcined to 500 °C. (b) Subsequent TRP after ammonia admission.

The TPR profile *a* of the sample calcined to 500 °C, shown in fig. 2 indicates that hydrogen consumption was complete at 200 °C. A separate TPR from −80 °C to 500 °C did not show $H_2$ consumption above 200 °C. However, after the same sample was neutralized with ammonia, the subsequent TPR profile *b* shows additional hydrogen consumption. This additional hydrogen consumption is attributed to the reduction of $Rh^+$ to $Rh^0$ after the protons, formed as described by eq. (2), have been trapped by $NH_3$. The oxidation state of Rh supported in faujasite zeolite has also been investigated by Kevan et al. [32]. Their ESR spectra of Rh/NaX calcined to low temperature showed the presence of two species; $Rh^+$ cations and a species which they attributed to $Rh^{2+}$ cations. However, with the present TPR data, we would interpret that ESR signal as a Rh° signal. Additional support of this conclusion is provided by our IR spectra.

The TPO data show that calcination to 200 °C will still leave $NH_3$ coordinated with the $RH^{3+}$ cations. During the reduction process, the ammine ligands are released and thus can form $NH_4^+$ ions with the protons. The effect of this thermodynamic sink becomes evident from a comparison of figs. 3 and 4. The FTIR spectra of $Co_{ads}$ on Rh/NaY(500/250) and Rh/NaY(200/250) are dramatically different. Figure 3 shows bands at 2114, 2100, 2047, and 2027 $cm^{-1}$ that were assigned by Primet et al. [19,29] to $Rh^+(CO)_2$, and bands at 2131, 2090, and 1828 $cm^{-1}$ that were assigned by Lefebvre et al. [38] to Rh carbonyl clusters.

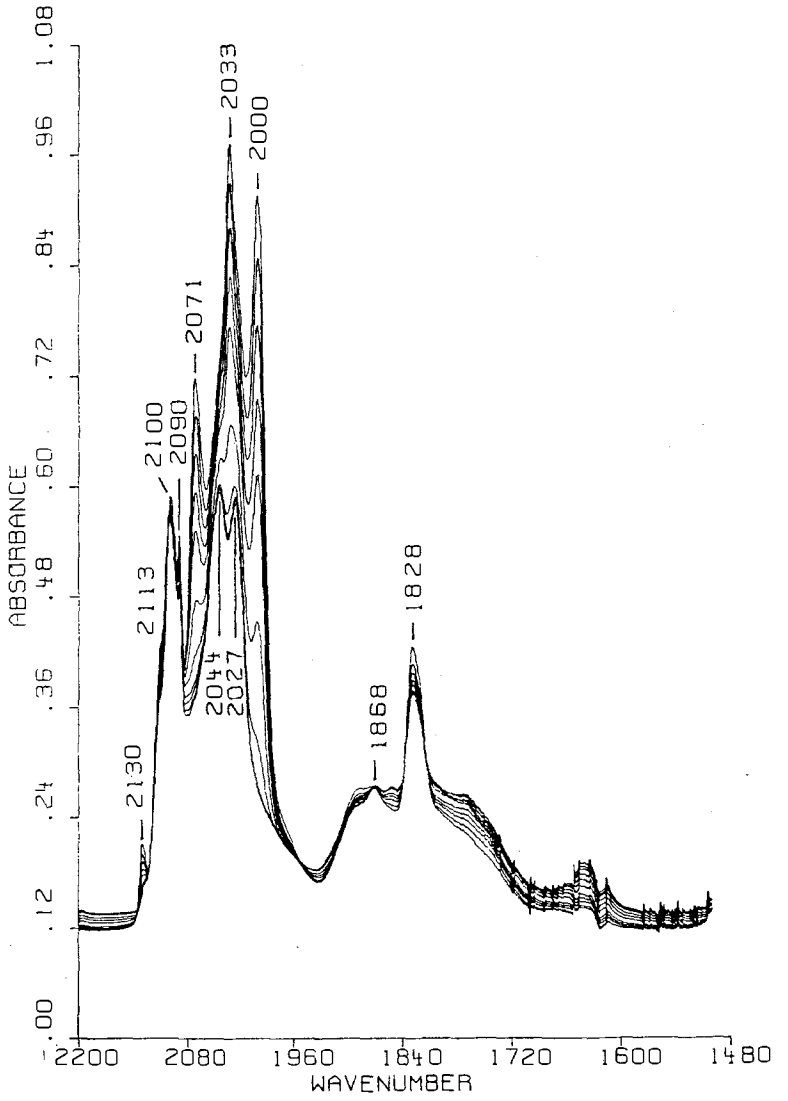


Fig. 3. FTIR spectra of CO adsorbed on reduced Rh/NaY(500/250); Purging time (min): 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180.

Figure 4 shows that in the presence of $NH_3$ new bands at 2072, 2033, and 2000 $cm^{-1}$ dominate the spectrum. This striking difference is attributed to the additional reduction of $Rh^+$ cations to Rh atoms in an environment of $NH_3$. In accordance with Primet et al. [29], these bands at 2072, 2033, and 2000 $cm^{-1}$, which have apparently not been reported before for Rh/NaY, can be attributed to the linear mode of CO adsorbed on Rh particles. Table 1 lists the band assignments.

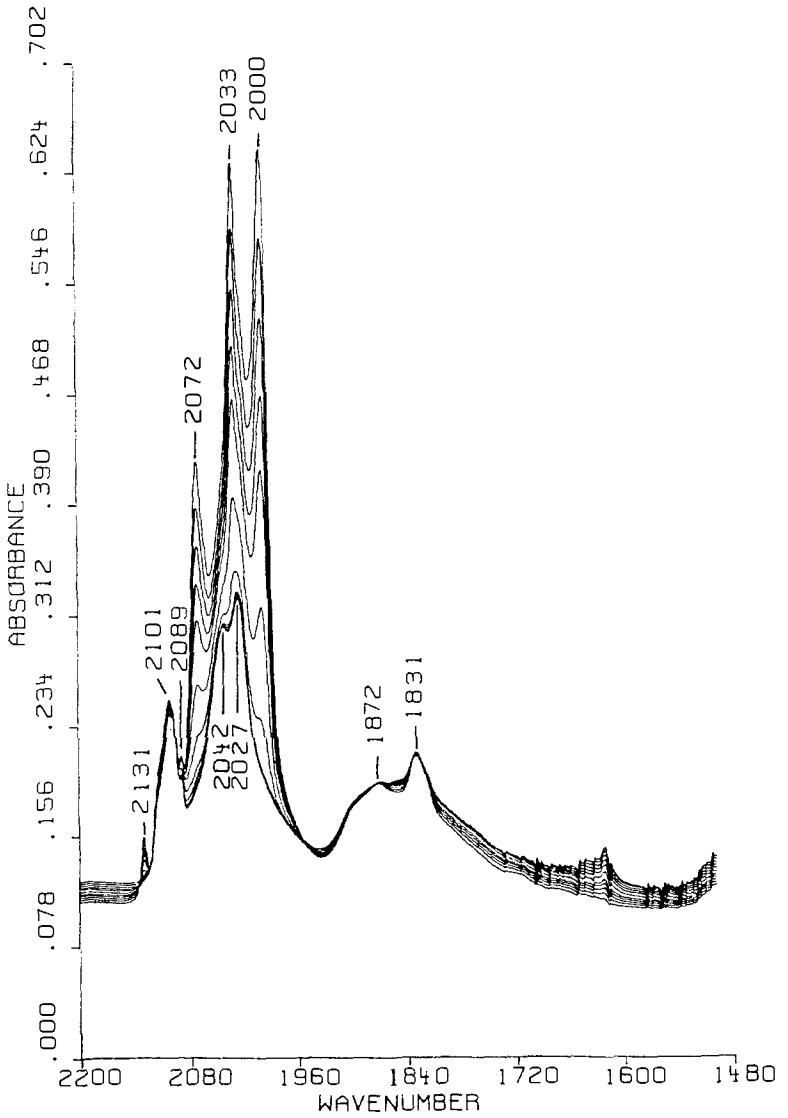


Fig. 4. FTIR spectra of CO adsorbed on reduced Rh/NaY(200/250); Purging time (min): 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180.

Garland and Yang [21] reported the presence of bands at 2033 and 2002 $cm^{-1}$ which were attributed to $Rh_2(CO)_4Cl_2$. They showed a spectrum with a strong 2033 $cm^{-1}$ band and a weak 2002 $cm^{-1}$ band. However, in fig. 4, it is evident that both of these bands are strong. Moreover, Garland and Yang showed that the strong 2033 $cm^{-1}$ band was coupled with a strong 2088 $cm^{-1}$ band. This relationship is not seen in fig. 4. The 2089 $cm^{-1}$, which is present in fig. 4, is weak and is attributed to the Rh carbonyl cluster, which has corresponding bands at 2131 and 1831 $cm^{-1}$. These differences, therefore, suggest that these bands at

2033 and 2000 $cm^{-1}$ are not due to $Rh_2(CO)_4Cl_2$, but rather to linearly bonded CO on Rh particles.

Another remarkable difference between figs. 3 and 4 becomes apparent as the bands at 2072, 2033, and 2000 $cm^{-1}$ decrease in intensity due to CO desorption, during purging with Ar at room temperature, leaving only the bands attributed to $Rh^+(CO)_2$ and to the Rh cluster. After 3 hours or purging, CO desorption from the Rh particle was complete and the final spectrum in fig. 4 looks similar to the spectra in fig. 3, although the relative intensities are different. This difference is likely due to the reduction and growth of Rh particles.

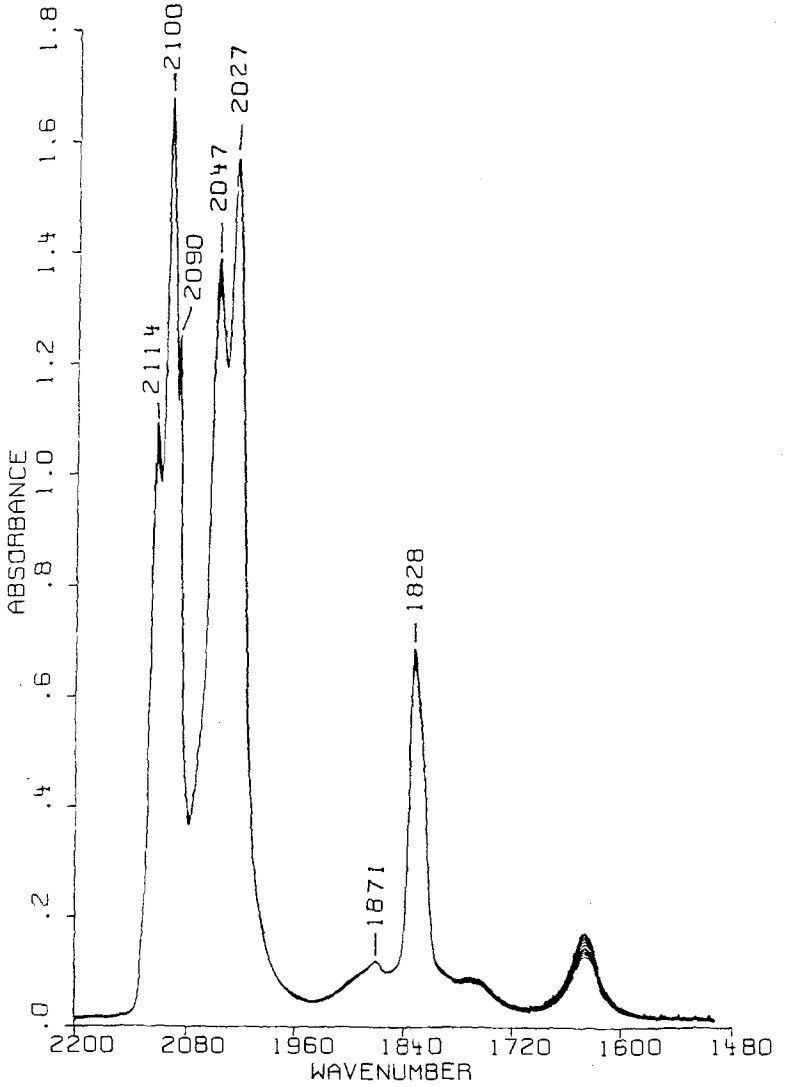


Fig. 5. FTIR spectra of CO adsorbed on neutralized/reduced $Rh/NaY_{NH_3}(500/250)$; Purging time (min): 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180.

It is also interesting to note that complete CO desorption at room temperature was not attained. In particular, CO desorption at room temperature from the $Rh^+$ cation was never observed, which is in agreement with results obtained by Takahashi et al. [39]. However, it was observed that upon further readmission of CO, the bands at 2072, 2033, and 2000 $cm^{-1}$ reappeared; adsorption on and desorption of CO from the Rh particles were completely reversible.

The presence of the Rh particles is also apparent from the FTIR spectra of $Co_{abs}$ on $Rh/NaY_{NH_3}$ (500/250) (fig. 5). Note that the original ammine groups were destroyed at 500 °C, but $NH_3$ was added to bind the protons created, as described by eqs. (2) and (3), and the neutralized sample was reduced again. Figures 4 and 5 are similar because of the presence of ammonia within both samples during reduction. However, figs. 3 and 5 are dramatically different because no ammonia was present during the reduction of the sample of fig. 3.

## 4. Conclusions

The presence of Rh particles in NaY has profound implications on the redox chemistry of rhodium. CO adsorption does not lead to the reoxidation of $Rh^0$ particles to $Rh^+$ cations. Instead, the reducibility of rhodium in zeolites is largely controlled by the concentration of protons. For high proton concentrations, a significant portion of Rh is not reduced beyond $Rh^+$, a species which readily forms $Rh^+(CO)_2$ with gaseous CO. In the presence of ammonia, Rh is completely reduced to $Rh^0$ because $NH_3$ acts as a thermodynamic sink to the protons. The TPR and TPO profiles, in conjunction with the $Co_{ads}$ FTIR spectra, provide spectroscopic evidence for the formation of highly dispersed Rh in NaY.

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