

Adsorption of Molecular Nitrogen on Rhodium Supported on Dealuminated Zeolite Y; the Formation of well-defined Surface Dinitrogen Complexes

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The surface complexes $\text{Rh}^{\text{I}}(\text{CO})(\text{N}_2)^+$ with $\nu(\text{CO})$ 2062 cm^{-1} and $\nu(\text{N}_2)$ 2252 cm^{-1} and $\text{Rh}^{\text{I}}(\text{N}_2)_2^+$, $\nu(\text{N}_2)$ 2244 + 2218 cm^{-1} , which are stable in flowing nitrogen up to 250 °C, have been synthesised from $\text{Rh}^{\text{I}}(\text{CO})_2^+$ on highly dealuminated zeolite Y (DAY, US-Ex).

Several transition-metal complexes containing dinitrogen as ligands are known and attempts have been made to utilise these complexes as models for nitrogen fixation.¹ However, the interaction of molecular nitrogen with transition metals has been found to be weak and the adsorption of N_2 on supported metal catalysts has been observed, therefore, generally at low temperature and/or at high pressures. For supported Rh, an interaction with molecular nitrogen has been observed also at higher temperatures for Rh on TiO_2 .^{2,3} and for alkali-promoted catalysts,⁴ but these interactions were found to occur rather with partially-reduced TiO_2 ³ or with the alkali promoter.⁵ Similarly, the IR band at 2063 cm^{-1} , which was detected during the interaction of molecular nitrogen with a Rh-containing NaY zeolite at 200–400 °C, was suggested to be the result of a reaction with the sodium component.⁶ The adsorption of N_2 on supported Rh at low temperature^{7,8} or at high pressures^{9,10} have been studied by IR spectroscopy. The surface species found by Wang and Yates⁸ and by Wey *et al.*^{9,10} on $\text{Rh}/\text{Al}_2\text{O}_3$ show IR bands at 2301 and 2276 cm^{-1} that were assigned to $\text{N}_2/\text{Rh}^{\delta+}$ and at 2256 cm^{-1} assigned to N_2/Rh^0 .

Here we report on the formation of well-defined dinitrogen complexes of rhodium supported on highly dealuminated Y zeolites. These complexes are stable at temperatures up to 250 °C in nitrogen at atmospheric pressure.

Previously we showed that dealuminated Y zeolite (US-Ex, DAY) is a unique material to stabilise well-defined surface complexes of transition metals. Subcarbonyls of Rh,^{11–13} Ru and Ir¹⁴ and mixed carbonyl-nitrosyls of Rh^{13,15} could be identified and, due to the unusual sharpness of the IR bands, structurally characterised. In the present work we show that

these well-defined surface species can be used as the starting material to the synthesis of other well-defined surface complexes.

Rh/DAY and Rh/US-Ex (1% m/m Rh) was prepared by impregnating the supports DAY (Si:Al > 100, kindly supplied by DEGUSSA, obtained by exchange of the Al atoms for Si by treating the NaY with SiCl_4 ¹⁶) or US-Ex (Si:Al ~ 100, obtained by hydrothermal treatment of NH_4Y ¹⁷) with an appropriate amount of RhCl_3 in ethanolic solution and drying the sample at 120 °C in air. The transmission IR studies were performed with self-supported wafers using a special IR cell made from stainless steel for *in situ* measurements up to 400 °C and 50 bar, connected to a gas flowing system, which allows a fast variation of the feed gas. The spectra were recorded with a FTIR spectrometer (BIORAD FTS 60A) at 2 cm^{-1} resolution.

In a first step, Rh dicarbonyl $\text{Rh}^{\text{I}}(\text{CO})_2^+$ was formed on the cation positions of DAY by treating the sample in a flow of $\text{CO}(5\%)/\text{Ar}$ at 150 °C. In the IR spectra, strong bands at 2118 and 2053 cm^{-1} appear and, simultaneously, the intensity of the OH-bands at 3630 (HF) and 3567 cm^{-1} (LF) of the acid hydroxyls decreases.¹² Subsequent treatment of the dicarbonyl in a flow of H_2/N_2 at 200 °C results in partial decarbonylation as indicated by the decreasing intensity of the corresponding IR bands at 2118 and 2053 cm^{-1} . At the same time, a new carbonyl species is formed with a carbonyl stretching vibration at *ca.* 2090 cm^{-1} [Fig. 1(a)]. This monocarbonyl is stable in argon or in vacuum at room temp., but highly reactive with CO yielding again the dicarbonyl.

This surface monocarbonyl is also reactive towards molecular nitrogen. Fig. 1(b) shows the IR spectra after switching the gas feed at 200 °C from H_2/N_2 to pure nitrogen and cooling the sample down to room temp. The band at *ca.* 2090 cm^{-1} of the monocarbonyl decreases and new bands in the dinitrogen and carbonyl stretching region appear. The wavenumbers of these bands at room temp. are shown in Table 1. A correlation analysis of the integrated absorbances of the corresponding bands in a series of experiments suggests that there are at least two well-defined surface complexes with dinitrogen as ligands: a mixed dinitrogen-carbonyl complex with IR bands at 2252 and 2062 cm^{-1} and a complex with two nitrogen stretching bands at 2244 and 2218 cm^{-1} , most probably a surface complex with two dinitrogen ligands. Besides these nitrogen containing complexes, the increasing IR band at 2014 cm^{-1} , which is already observed in Fig. 1(a), should be assigned to another monocarbonyl species and the $\text{Rh}^{\text{I}}(\text{CO})_2^+$ dicarbonyl is also present (bands at 2118 and 2053 cm^{-1}). It is interesting to note that the spectrum as shown in Fig. 1(b) does not differ markedly from that taken at 200 °C. The only significant

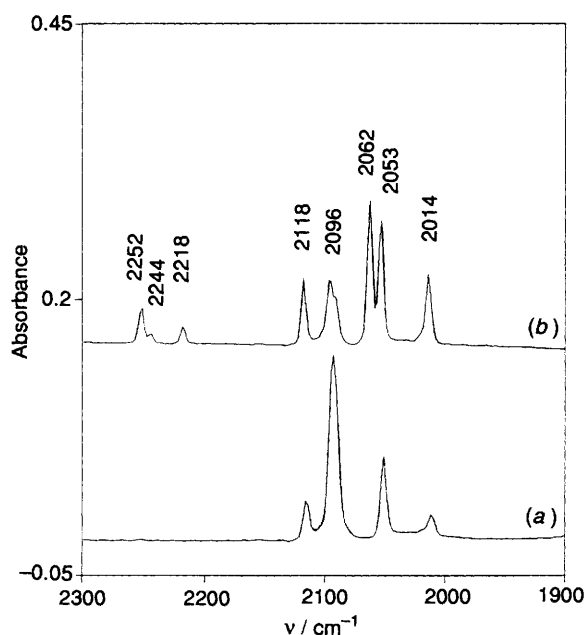


Fig. 1 IR spectra of Rh/DAY in the nitrogen and carbonyl stretching regions after interaction of surface $\text{Rh}^{\text{I}}(\text{CO})_2^+$ (a) with a flow of H_2/N_2 at 200 °C and (b) the subsequent interaction with pure N_2 and cooling down to 30 °C

Table 1 ν (cm^{-1}), force constants (N/m) and assignments of surface complexes on Rh/DAY

$\nu(\text{N}_2)$	$\nu(\text{CO})$	Assignment	$k(\text{N}_2)$	$k(\text{CO})$
2252	2062	$\text{Rh}^{\text{I}}(\text{CO})(\text{N}_2)^+$	2092	1718
2244 + 2218		$\text{Rh}^{\text{I}}(\text{N}_2)_2^+$	2053	
	2118 + 2053	$\text{Rh}^{\text{I}}(\text{CO})_2^+$		1757
	2096	$\text{Rh}^{\text{I}}(\text{CO})^+$		1775
	2014	Rh monocarbonyl		1639

difference (beside a small shift of the band maxima) is that the monocarbonyl with the band at 2096 cm^{-1} seems to raise at the expense of the monocarbonyl with $\nu(\text{CO})$ at 2014 cm^{-1} at decreasing temperature. The nitrogen complexes are stable in flowing nitrogen, but react immediately with CO to give the Rh dicarbonyl.

The assignment of the IR bands was verified by experiments using isotopic mixtures containing C^{18}O or $^{15}\text{N}_2$. For the formation of C^{18}O containing species it was necessary to start from the dicarbonyl already exchanged with C^{18}O . The corresponding C^{18}O component of the reactive monocarbonyl has a stretching band at 2047 cm^{-1} . The spectra of the surface species after the interaction with pure N_2 are shown in Fig. 2.

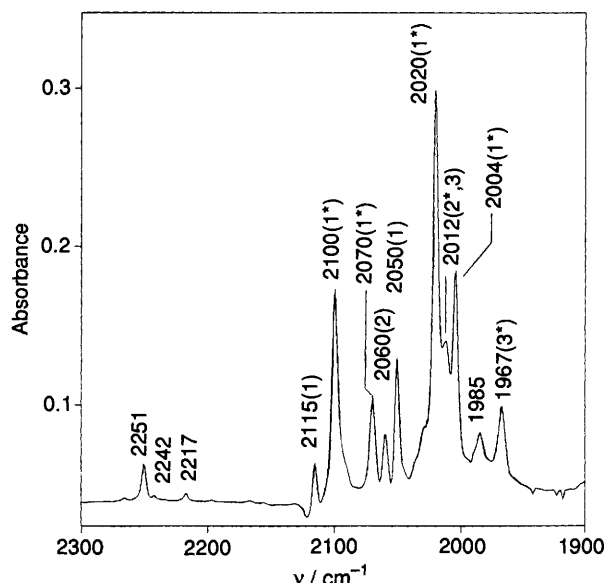


Fig. 2 IR spectra of Rh/US-Ex in the nitrogen and carbonyl stretching regions after interaction of surface $\text{Rh}^{\text{I}}(\text{CO})_2^+$ (with an isotopic composition of ca. 50% C^{18}O) with a flow of H_2/N_2 and a subsequent interaction with pure N_2 at 250°C . The species containing C^{18}O are indicated by asterisks: (1) $\text{Rh}(\text{CO})_2$, (2) $\text{Rh}(\text{N}_2)(\text{CO})$ and (3) monocarbonyl.

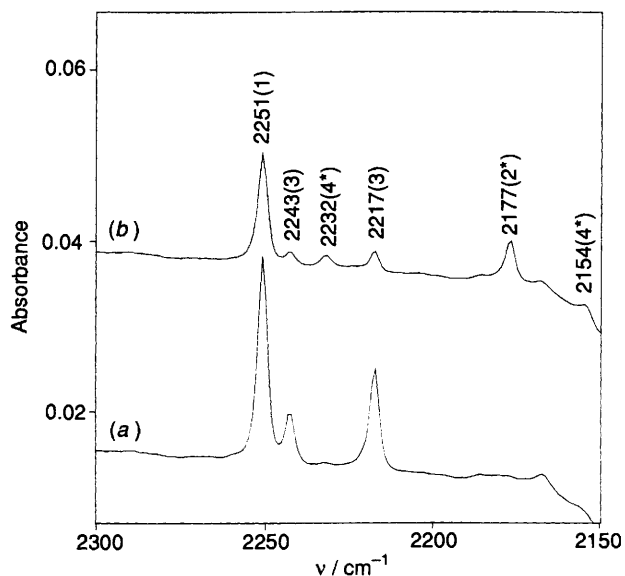


Fig. 3 IR spectra of Rh/DAY in the nitrogen stretching region after the formation of the surface dinitrogen complexes (a) as in Fig. 1(b) and (b) after a subsequent addition of ca. 25% $^{15}\text{N}_2$ to the N_2 stream at 200°C . The species containing $^{15}\text{N}_2$ are indicated by asterisks: (1) $\text{Rh}(^{14}\text{N}_2)(\text{CO})$, (2) $\text{Rh}(^{15}\text{N}_2)(\text{CO})$, (3) $\text{Rh}(^{14}\text{N}_2)_2$ and (4) $\text{Rh}(^{14}\text{N}_2)(^{15}\text{N}_2)$.

The CO bands of the monocarbonyls are doubled, as should be expected, with a difference of $46\text{--}48\text{ cm}^{-1}$ between the C^{16}O and the C^{18}O bands. Fig. 3 shows the IR spectra of the dinitrogen-containing surface species before and after the addition of ca. 25% $^{15}\text{N}_2$ to the nitrogen stream. The new bands in spectrum (b) are shifted by 74 cm^{-1} with respect to the parent ones (in the case of the mixed-surface compound $\text{Rh}^{\text{I}}(^{14}\text{N}_2)(^{15}\text{N}_2)^+$ the sum of the symmetric and the antisymmetric stretching modes) as should be expected for the proposed assignment.

The two supports used have the same crystal structure and a similar Si:Al ratio, but differ significantly in the mesopore structure. Owing to the different dealumination procedure, US-Ex has a high amount of mesopores and, consequently, a higher amount of terminal silanol groups as compared with DAY.¹⁷ The formation and the properties of the well-defined surface species described in the present work are, nevertheless, similar for both supports. This is an argument in favour of the formation of these species at the cation positions rather than on the outer surface or in the mesopores of the zeolite.

Table 1 also summarises the force constants of the $\text{N}\equiv\text{N}$ and the $\text{C}\equiv\text{O}$ stretching vibrations obtained in the framework of an approximate force field.¹⁸ It is interesting to note that $k(\text{CO})$ is lower and $k(\text{N}_2)$ is higher in the mixed-complex $\text{Rh}^{\text{I}}(\text{CO})(\text{N}_2)^+$ as compared with the dicarbonyl or the bis-dinitrogen complex, respectively. This is consistent with the competition of the stronger π -acceptor CO with dinitrogen for bonding electrons.

Received, 25th November 1993; Com. 3/07027A

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