

On the Clarification of the IR Stretching Vibration Assignment of Adsorbed N₂ on Rh⁰ and Rh^{δ+} Surface Atoms of Supported Rh Crystallites

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Received: February 20, 2006; In Final Form: March 17, 2006

The low-temperature adsorption of N₂ on Rh/SiO₂ samples of various particle-size distributions was followed by FTIR. The addition of O₂ pulses on Rh⁰ surfaces saturated with chemisorbed N₂ allowed us to reassign stretching frequencies attributed originally to N₂–Rh⁰ to N₂–Rh^{δ+}. The formation of the latter oxidized Rh species is assumed to be induced by an electron withdrawal from adsorbed oxygen species on Rh surface centers neighboring those onto which N₂ species are chemisorbed. The present work, thus, enables us to delimit ranges of frequencies for which the adsorption of N₂ can be considered to occur on either Rh⁰ or Rh^{δ+} centers for ν_{N_2} lower or higher than 2243 cm⁻¹, respectively. The N₂-FTIR experiments performed on the studied catalysts also suggest a lattice plane selectivity for N₂ adsorption on metallic Rh planes of different natures which, to our knowledge, has not been reported yet for Rh.

1. Introduction

The characterization of the active sites of supported catalysts is one of the most challenging tasks that still attract much attention in catalytic studies. In this objective, the adsorption of probe molecules followed by FTIR is of the greatest interest.¹ Among the probes, CO has received much interest and has been used intensively for the determination of the oxidation state of supported transition metals due to its capability to form metal carbonyls.² CO, however, is not harmless with respect to the probed surfaces as it might alter the catalytic sites by dissociation on metal surfaces² or reduce the active sites on which the adsorption occurs. Moreover, in the case of supported Rh catalysts, it has been demonstrated that CO might also lead to the oxidative disruption of small Rh metallic clusters to Rh^I-(CO)₂, the evidence of which has been provided initially by Van't Blick et al.³ By means of extended X-ray absorption fine structure spectroscopy (EXAFS), these authors have shown that the size of the Rh clusters decreases with the introduction of CO. Two years later, Solymosi and Pástor reported the first IR spectra supporting the strong interaction of Rh⁰ crystallites with CO and their subsequent oxidative disruption.⁴ Such a disruption phenomenon was then confirmed by several other groups on various supported Rh catalysts.^{5–8} More recently, the STM pictures reported by Solymosi and co-workers definitely prove the oxidative disruption of Rh⁰ crystallites, supported in this case on a TiO₂ single crystal, upon CO exposure.⁹ It has also been shown that this disruption process is assisted by the hydroxyl groups, neighboring the Rh clusters, of the zeolite-exchanged materials^{6,8} or the SiO₂-supported⁷ and Al₂O₃-supported^{3–5} Rh catalysts.

To overcome these problems, the use of a nonreactive probe molecule such as N₂ might be considered. Compared with CO, the number of studies which have investigated the N₂-FTIR of Rh materials is much more restricted.^{10–15} In these studies, it is worthwhile to note that the intensity of the IR features is

fairly low. Two reasons account for this limited number of studies: (i) as N₂ very weakly interacts with transition metals, its adsorption is preferably carried out at low temperatures^{10,11,13} or at RT but at high pressures of N₂,^{14,15} which are technically more demanding experimental conditions; (ii) the molar extinction coefficient of adsorbed N₂ is much lower than that of CO.¹³ On the other hand, as gaseous N₂ is not IR active,¹⁶ the recorded IR spectra are not influenced by the gas phase.

From the aforementioned studies, an overall agreement has been reached on the attribution of the band observed at about 2300 cm⁻¹ to N₂ chemisorbed on Rh^{δ+} species of Rh/Al₂O₃ catalysts.^{13–15} In contrast, the assignment of the stretching vibration of N₂ bonded to Rh⁰ surface atoms has been reported in a very broad range of frequencies from 2154 to 2276 cm⁻¹.^{10–15}

This work aims at shedding light on the origins of this widespread distribution of frequencies reported for N₂ bonded to Rh⁰ atoms and to delimit ranges of wavenumbers for which the adsorption of N₂ occurs on Rh⁰ or Rh^{δ+} atoms. The lattice plane-selectivity aspect of N₂ adsorption on Rh⁰ is also discussed.

2. Experimental Section

Catalyst Preparation. The Rh/SiO₂ catalysts (0.7 or 4.8 wt % Rh) were prepared by incipient wetness impregnation of a silica (Degussa, Aerosil 50, 50 m² g⁻¹) support by an aqueous solution of RhCl₃ · 3H₂O. After aging for 12 h, the catalysts were dried at 120 °C for 3 h in air. Rh contents were determined by chemical analyses (CNRS, Vernaison, France). These catalysts are referred to as Rh(wt % metal content)/SiO₂.

Titration of Adsorbed Oxygen by Hydrogen. The percentage of exposed zerovalent Rh atoms of the Rh/SiO₂ catalysts was determined by O₂–H₂ titration, on pulse chemisorption equipment (Micromeritics AutoChem 2910), following the procedure reported by Guglielminotti et al.¹⁷ Before titration, the catalyst sample (0.100 or 0.020 g) was treated at 500 °C in a stream of H₂ (25 cm_{NTP}³ min⁻¹) for 2 h and then in a stream

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of He ($25 \text{ cm}^3_{\text{NTP}} \text{ min}^{-1}$) for 30 min. The temperature was then decreased to 100 °C under He and the catalyst was saturated with chemisorbed oxygen with pulses of O_2 (5% O_2 in He). The titration of the chemisorbed oxygen species by pulsed- H_2 was then performed at 100 °C. This temperature allowed for desorption of H_2O formed in the course of titration.¹⁸ The estimation of the percentage of metal exposed (PME) was done assuming the following chemisorption stoichiometries: $\text{H/Rh}^0 = 1$ and $\text{O/Rh}^0 = 1.5$.^{17,18} The mean particle diameter was calculated as¹⁹

$$d = 6(v_m/a_m)/\text{PME}$$

where d , v_m , a_m , and PME are the mean particle diameter (Å), the volume occupied by a Rh atom in bulk metal (13.78 Å^3), the area occupied by one Rh surface atom (7.58 Å^2), and the percentage of metal exposed (%), respectively.

Transmission Electron Microscopy. The Rh/SiO₂ pre-reduced catalysts were also characterized by means of transmission electron microscopy (TEM) with a JEOL 2010 UHR instrument. The microscope was operated at 100 kV with a tungsten filament. The powered catalyst was embedded in epoxy resin and cut into thin slices (70 nm) with an ultramicrotome equipped with a diamond knife. The particle-size distributions of the Rh/SiO₂ catalysts were estimated by counting about 600 metallic particles on each sample.

XRD (X-ray Diffraction). The XRD pattern of the pre-reduced Rh(4.8)/SiO₂ sample was obtained on a SIEMENS D500 diffractometer with a Cu K α monochromatized radiation (0.1548 nm) operated at 300 kV and 300 mA. The mean diameter of the Rh particles was estimated from the Scherrer formula applied to the diffraction peak observed at about 41°, which corresponds to the Rh(111) plane (JCPDS file 05-685).

Low-Temperature N₂ Adsorption Followed by FTIR. Fourier transform infrared (FTIR) spectra of adsorbed N₂ on the SiO₂-supported Rh samples were collected on a Bruker Vector 22 FTIR spectrometer equipped with a liquid N₂-cooled MCT detector and a data acquisition station. 256 scans were averaged with a spectral resolution of 2 cm^{-1} .

The samples were pressed into self-supporting wafers of about 12 mg cm^{-2} . The wafers were loaded in a moveable glass sample holder, equipped on top with an iron magnet, and inserted in a conventional Pyrex-glass cell (CaF₂ windows) connected to a vacuum system. The iron magnet allowed for the transfer of the catalyst sample from the oven-heated region to the infrared light beam. The glass cell was placed in a polystyrene container that allowed the sample to be cooled to a temperature of about 100 K with liquid N₂.

Prior to N₂ adsorption, the catalysts were submitted to a dynamic ($50 \text{ cm}^3 \text{ min}^{-1}$) reducing pretreatment (5% H₂ in Ar, Air Liquide, 99.999%) at 500 °C for 2 h at atmospheric pressure. The samples were then evacuated (7.5×10^{-7} Torr, 1 Torr = 133.3 Pa) at 500 °C for 60 min. Finally, the temperature was decreased to 100 K under dynamic vacuum. To ensure an adequate cooling of the sample, a pulse of 0.2 μmol of He (Air Liquide, 99.999%) was introduced.

Considering the Rh(4.8)/SiO₂ samples, increasing pressures of N₂ (Air Liquide, 99.999%), trapped at 77 K, were introduced up to 14 Torr. As will be shown, this does not influence the intensity of the absorption bands assigned to N₂ bonded to Rh⁰ surface atoms.

Pulses of O₂ (Air Liquide, 99.999%) were introduced on the N₂-preadsorbed samples contacted under a pressure of 14 Torr of N₂.

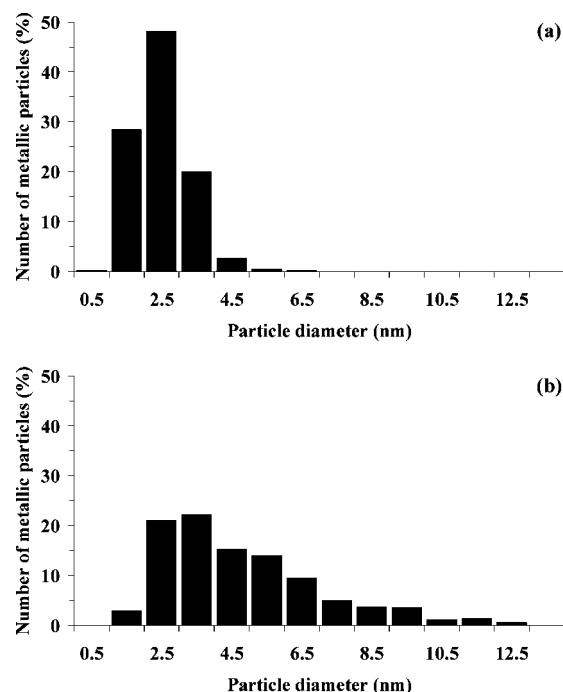


Figure 1. Particle-size distributions of (a) Rh(0.7)/SiO₂ and (b) Rh(4.8)/SiO₂.

TABLE 1: Characterization of the Rh/SiO₂ Catalysts

| Rh (wt %) | PME (%) ^a (O ₂ –H ₂ titration) | mean diameter (nm) | | |
|--------------|--|---|-----|-----|
| | | O ₂ –H ₂ titration | TEM | XRD |
| 0.7 | 51 | 2.1 | 2.5 | |
| 4.8 | 27 | 4.0 | 4.9 | 5.2 |

^a Percentage of metal exposed.

Unless specified otherwise, the spectrum at 100 K of the pretreated sample was used as a reference and subtracted from the spectra of the sample exposed to the different probe molecules. To compare band intensities from both samples, intensities have been normalized with respect to the sample weight. The curve-fit of the spectrum was performed with the Levenberg–Marquardt method from the Grams software (version 5.2, Galactic).

3. Results

Figure 1 shows the particle-size distributions of the studied Rh/SiO₂ samples. The particle-size distribution of Rh(0.7)/SiO₂ is rather narrow with a maximum peaking at 2.5 nm. On the other hand, that of Rh(4.8)/SiO₂ is much broader with a maximum shifted to bigger particle diameters. The mean particle diameters estimated from these TEM measurements are listed in Table 1. This table shows that the mean particle diameter of Rh(4.8)/SiO₂ is twice that estimated for Rh(0.7)/SiO₂. These mean particle diameters compare rather well with those determined by means of O₂–H₂ titration for Rh(0.7)/SiO₂ and by means of XRD for Rh(4.8)/SiO₂. For Rh(0.7)/SiO₂, the slightly lower mean particle diameter determined by means of O₂–H₂ titration compared with that measured by TEM might be reasonably attributed to the detection limit of the microscope. TEM analysis, thus, leads to a slight overestimation of the mean particle diameter by neglecting particles smaller than 1 nm. For Rh(4.8)/SiO₂, the mean particle diameter is greater when estimated by XRD compared with that estimated by TEM, which is not surprising as the smaller crystallites are scarcely taken

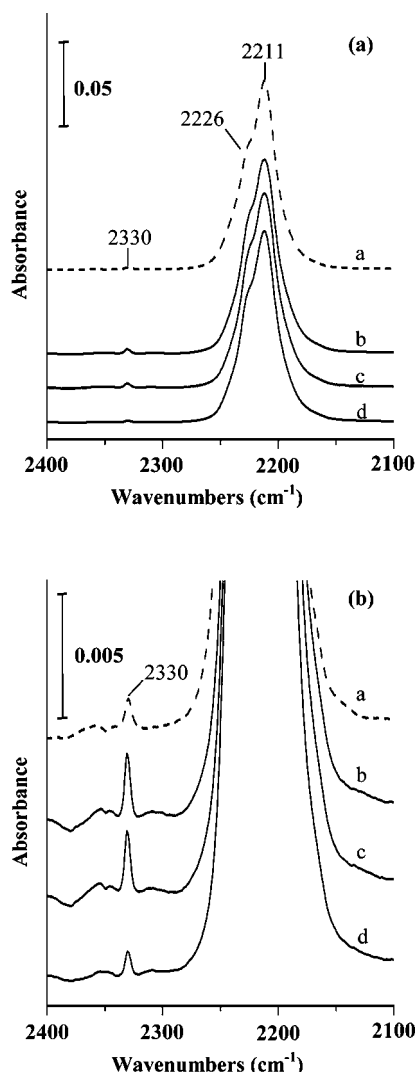


Figure 2. Influence of the pressure of N₂ introduced on Rh(4.8)/SiO₂ at 100 K: (a) 14.0, (b) 10.6, (c) 9.7, and (d) 2.9 Torr. (---) 1st and (—) 2nd sample.

into account by the Scherrer formula when the full-width at half-maximum intensity is considered.¹⁹

The adsorption of N₂ at 100 K, under various pressures of N₂, on two different prerduced samples of Rh(4.8)/SiO₂, first shows a good reproducibility (Figure 2a). These spectra display a narrow weak absorption band at 2330 cm⁻¹ and a broad intense one peaking at 2211 cm⁻¹. The latter band, which is assigned to the adsorption of N₂ on Rh⁰ surface atoms, is hardly influenced by the N₂ pressure, suggesting that the Rh⁰ surface is already almost fully saturated with adsorbed N₂ with a pressure of N₂ as low as 2.9 Torr (Figure 2a, spectrum d). From the comparison of spectra b–d of Figure 2b, one might conclude that the band at 2330 cm⁻¹ develops gradually with increasing pressures of N₂. This is clearly contradicted by spectrum a of Figure 2b, recorded under 14 Torr of N₂, which exhibits an absorption band at 2330 cm⁻¹ of a similar intensity as that observed in spectrum d of Figure 2b (2.9 Torr N₂). A kinetic interpretation of the development of this band is, thus, more likely, as spectra a and d were recorded less than 5 min after exposure of the samples to N₂. As reported in previous studies,^{13–16} this band is attributed to N₂ physisorbed on the OH groups of SiO₂. This weak interaction is confirmed by the features observed in the OH stretching region (not shown) for which the band assigned to isolated silanols⁷ at 3747 cm⁻¹ is

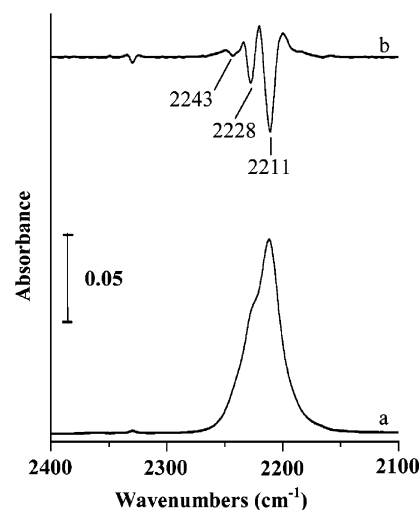


Figure 3. Low-temperature (100 K) infrared spectra of the Rh(4.8)/SiO₂ catalyst after adsorption of (a) N₂ at a pressure of 14.0 Torr and (b) the corresponding second derivative.

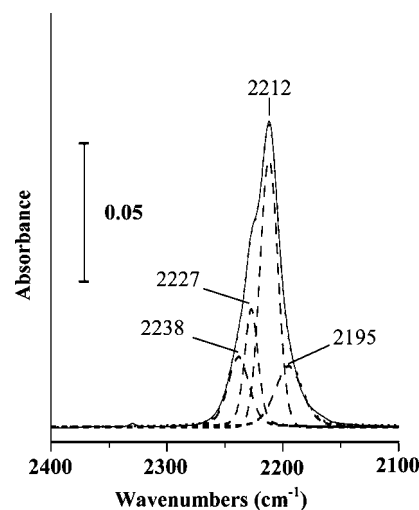


Figure 4. Decomposition of the spectra obtained on Rh(4.8)/SiO₂ after introduction of a pressure of 14 Torr of N₂ at 100 K: —, experimental data; ---, decomposed peaks; ···, curve-fit with four Gaussian–Lorentzian peaks.

shifted to 3713 cm⁻¹ with the introduction of N₂. In addition, the frequency of 2330 cm⁻¹ corresponds to that of the stretching frequency of N₂ gas.²⁰ The much higher shift in wavenumbers ($\Delta\nu = -118$ cm⁻¹) observed for the band peaking at 2211 cm⁻¹ supports the chemisorption of N₂ on Rh⁰ atoms. Compared to the band at 2330 cm⁻¹, the band at 2211 cm⁻¹, with an obvious shoulder at 2226 cm⁻¹, is much broader (2260–2150 cm⁻¹). This might be ascribed to the presence of Rh sites of heterogeneous composition. The second derivative of spectrum a from Figure 2 is shown in Figure 3. This second derivative clearly reveals the presence of absorption contributions at 2330, 2243, 2228, and 2211 cm⁻¹. The broad band peaking at 2211 cm⁻¹ of spectrum a (Figure 3) might be fitted satisfactorily with three Gaussian–Lorentzian peaks at 2238, 2227, and 2212 cm⁻¹ and an additional absorption band at 2195 cm⁻¹ (Figure 4).

When O₂ is pulsed on the sample maintained under 14 Torr of N₂ (Figure 5, spectra b–e, g–m), the band at 2330 cm⁻¹ is not modified at all. In contrast, the intensity of the bands at 2211 and 2226 cm⁻¹ decreases substantially without shifting and vanishes after the introduction of a cumulated pulsed quantity of O₂ of about 0.84 μ mol. The absence of shift with decreasing coverages of N₂ suggests that N₂ intermolecular

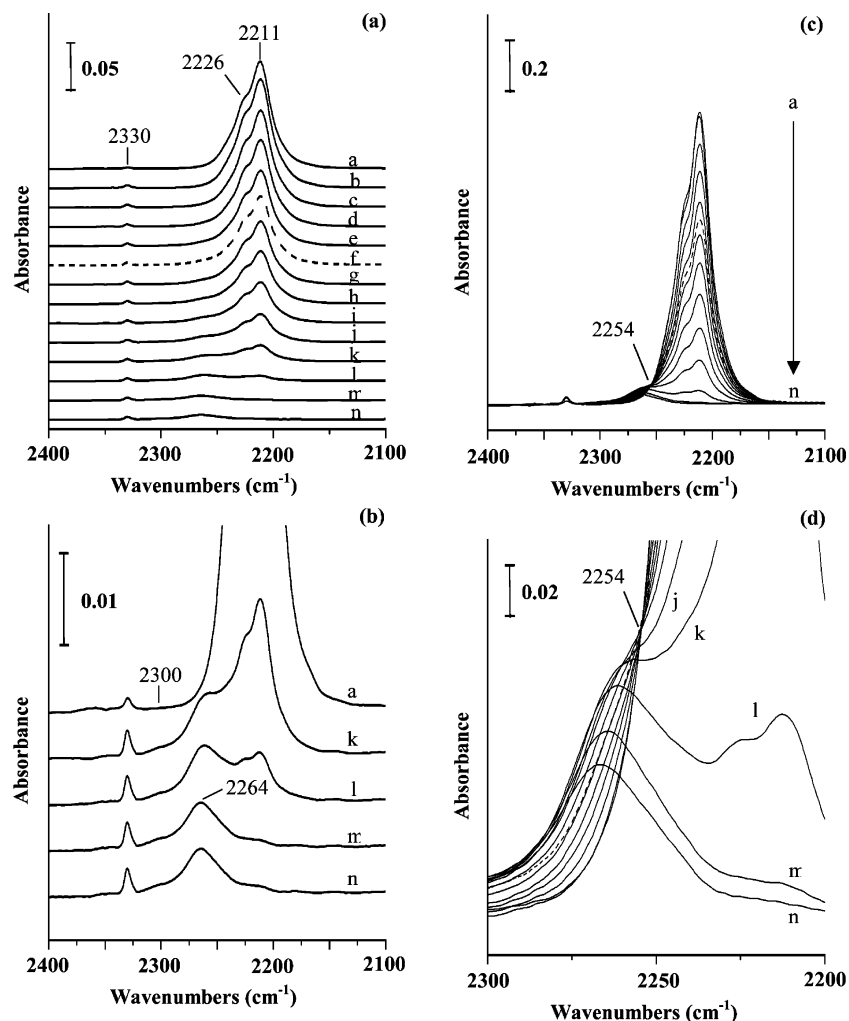


Figure 5. Low-temperature (100 K) infrared spectra of the Rh(4.8)/SiO₂ catalyst after adsorption of (a) N₂ at a pressure of 14.0 Torr and (b–e, g–n) subsequent pulses of 0.08 μ mol of O₂. Spectrum f (---) was recorded 12 min after measurement of spectrum e without introduction of a new pulse of O₂.

interactions are small, as also reported in previous studies.^{13,14} Spectrum f from Figure 5 deserves special comments. This spectrum was recorded 12 min after introduction of pulse e. Although additional O₂ was not introduced, the intensity of the band at 2211 cm⁻¹ decreases (Figure 5c). This suggests that the evolution of the N₂ IR features upon O₂ adsorption is a relatively slow process under the present experimental conditions. Interestingly, as the intensity of the band at 2211 cm⁻¹ decreases, a broad IR feature of low intensity emerges with a maximum at 2264 cm⁻¹ and a very weak shoulder at 2300 cm⁻¹ (Figure 5b, spectra k–n). It must be emphasized, however, that the low intensity of these high-frequency IR features are comparable to those reported in previous studies.^{13,14} The introduction of pulsed quantities of O₂ also clearly reveals the existence of an isosbestic point located at 2254 cm⁻¹ (Figure 5c,d).

The FTIR spectrum obtained on Rh(0.7)/SiO₂ after adsorption of N₂ at 100 K is shown in Figure 6 (spectrum a). As is the case for Rh(4.8)/SiO₂, a band at 2330 cm⁻¹ is observed, corresponding to physisorbed N₂ on the silanol groups of the support. This band is, however, more intense (Figure 6a) than for Rh(4.8)/SiO₂ (Figure 5a). This observation might be assigned to the lower coverage of SiO₂ by the Rh metallic phase and, thus, to an increase of the surface concentration of the silanol groups for Rh(0.7)/SiO₂. This conclusion is supported by the greater intensity of the band at 3747 cm⁻¹ on Rh(0.7)/SiO₂ (not

shown). As for Rh(4.8)/SiO₂, an intense band appears on Rh(0.7)/SiO₂ at 2212 cm⁻¹ (Figure 6a). In this case, however, the shoulder at 2225 cm⁻¹ is less obvious than in the case of Rh(4.8)/SiO₂. This clearly differentiates the shape of the absorption band at 2212 cm⁻¹ observed on the studied Rh/SiO₂ catalysts. Finally, the intensity of the broad band peaking at 2211 cm⁻¹ on Rh(4.8)/SiO₂ is about twice that observed on Rh(0.7)/SiO₂.

When pulsing O₂ (Figure 6, spectra b–e, g–j), the broad band at 2212 cm⁻¹ decreases without shifting and vanishes for a cumulated pulsed quantity of O₂ of about 0.27 μ mol (Figure 6b, spectrum i). As is the case on Rh(4.8)/SiO₂ (Figure 5), the introduction of O₂ leads to the appearance of a broad IR signal of weak intensity at 2262 cm⁻¹ and of a weak contribution at 2300 cm⁻¹ (Figure 6b). Finally, an isosbestic point also exists on Rh(0.7)/SiO₂ at 2257 cm⁻¹ (not shown).

4. Discussion

The low-temperature adsorption of N₂ on prereduced Rh/SiO₂ catalysts reveals a broad absorption band at 2212 cm⁻¹ (Figures 5 and 6). This absorption band, which can only be assigned to N₂ chemisorbed on zerovalent Rh surface atoms of Rh crystallites (Rh⁰), coincides with that reported by Yates et al.¹² on a Rh(10.0)/SiO₂ catalyst. This N₂ stretching frequency, however, differs slightly from that reported by Borod'ko and Lyutov¹⁰ for a Rh/SiO₂ catalyst (2236 cm⁻¹) and markedly from that

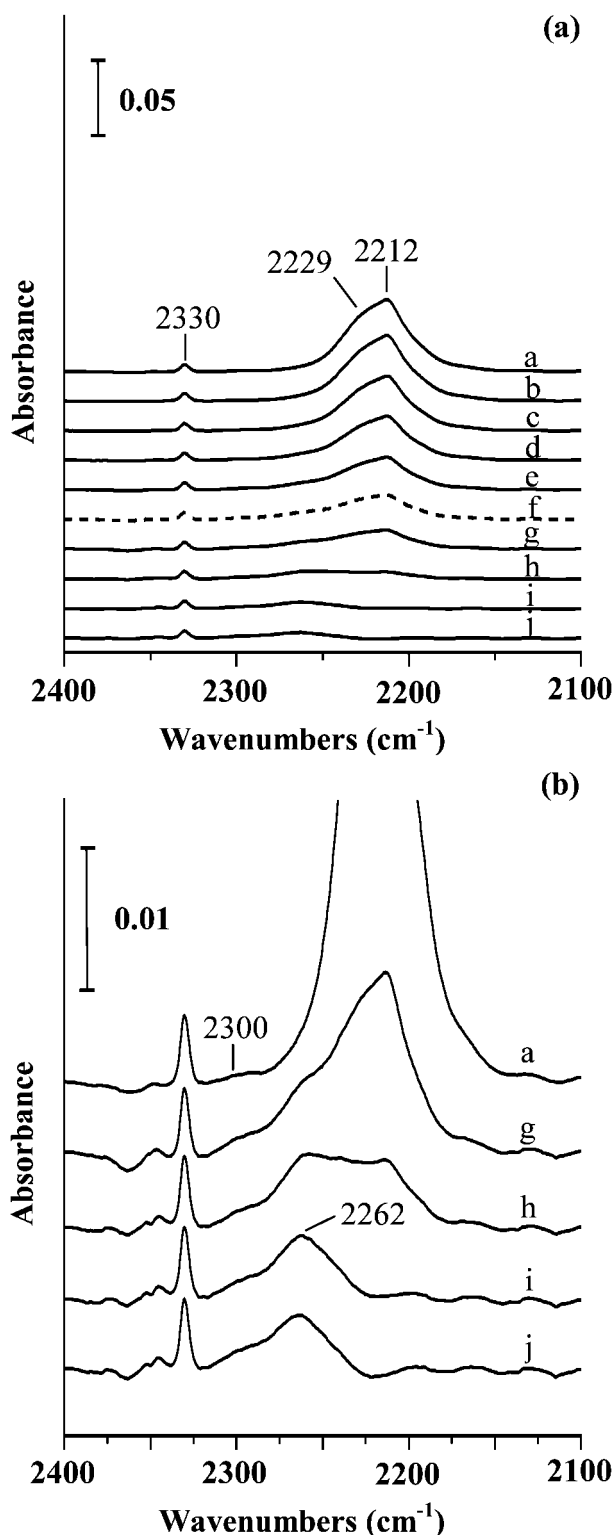


Figure 6. Low-temperature (100 K) infrared spectra of the Rh(0.7)/SiO₂ catalyst after adsorption of (a) N₂ at a pressure of 14.0 Torr and (b–e, g–j) subsequent pulses of 0.04 μmol of O₂. Spectrum f (---) was recorded 12 min after measurement of spectrum e without introduction of a new pulse of O₂.

reported by Wang and Yates or Worley and co-workers (2256–2257 cm⁻¹) for Rh(2.2)/Al₂O₃ samples.^{13–15} Although the study of Borod'ko and Lyutov¹⁰ was referenced by the latter authors, they did not comment on this 20 cm⁻¹ difference in frequency.

In addition to the absorption maximum at about 2212 cm⁻¹, the low-temperature adsorption of N₂ on the Rh/SiO₂ samples

shows an absorption contribution at about 2225 cm⁻¹ (Figures 5 and 6). The curve-fit of the broad absorption band also reveals the presence of two absorption contributions at 2238 and 2195 cm⁻¹ (Figure 4). In the present case, the absorption bands at frequencies higher than 2212 cm⁻¹ cannot be attributed to the adsorption of N₂ on Rh^{δ+}, as the samples were not submitted to oxidizing pretreatment^{13,14} and as it is well-established that transition metal clusters hardly interact with SiO₂. It must also be emphasized that the shape of the broad absorption band depends on the nature of the studied sample and, thus, on its particle-size distribution (Figure 1). Consequently, these bands are more likely attributable to N₂ chemisorbed on Rh⁰ atoms of exposed planes different from that responsible for the band at 2211 cm⁻¹. Changes in the electron work function upon N₂ adsorption at 77 K have, indeed, been revealed on various Rh model surfaces by Nieuwenhuys.²¹ It is worthwhile to report that these work function changes with the nature of the model surface must be correlated with the extent of electron back-donation from the metal to N₂ and, thus, to the position of N–N stretching frequency for N₂ adsorbed on transition metals.²¹ Such an assumption is further supported by the fact that N₂ adsorption has been demonstrated to be plane-selective on many transition metals, and more particularly on W.²² To our knowledge, the present study provides the first spectroscopic evidence of this lattice plane-selectivity aspect on Rh. According to this, the 2210–2236 cm⁻¹ range of frequencies (refs 10, 12 and this work) attributed to the stretching vibration of N₂ chemisorbed on Rh⁰ surface atoms of Rh crystallites supported on SiO₂ or Al₂O₃ might be understood reasonably with the preferential exposition of planes of different natures depending on the studied catalysts. This might also account for the elevated width of the N₂ absorption band revealed on the catalysts studied in the present work, and of previous studies,^{10,12} which most likely exhibit a wide variety of adsorption sites due to the polycrystalline nature of the Rh metallic phase when being supported on oxide carriers.

The preferential exposure of well-defined planes different from those of the catalysts studied in the present work or in previous studies,^{10,12} leading to N₂ stretching frequencies as high as 2256–2257 cm⁻¹,^{13–15} is less likely. The introduction of O₂ pulses on Rh⁰ surfaces saturated with chemisorbed N₂ species is very instructive on that particular point. On both Rh/SiO₂ samples (Figures 5 and 6), the gradual decrease of the band at 2212 cm⁻¹ with the introduction of O₂ shows that O₂ displaces adsorbed N₂ due to its much stronger bonding with Rh. More interesting is the concomitant appearance of a broad band of weak intensity with a maximum at 2262–2264 cm⁻¹ and a shoulder at 2300 cm⁻¹ (Figures 5b and 6b). The existence of isosbestic points at 2254 (Figure 5c,d) to 2257 cm⁻¹ suggests the transformation of one or more N₂ adsorbed species responsible for the absorption contributions at 2243 or/and 2228 cm⁻¹, the identification of which cannot be ascertained from the results of the present study, to N₂ adsorbed species in a new chemical environment resulting in the appearance of the broad absorption band at 2262–2264 cm⁻¹. From these results, it is obvious that the stretching vibration of adsorbed N₂ species shifts to higher frequencies with the introduction of O₂, and hence, when the remaining chemisorbed N₂ species become surrounded by oxygen species adsorbed on neighboring Rh⁰ surface atoms, as symbolized in Figure 7. In this figure, for the sake of simplicity, the chemisorption of O₂ is considered dissociative, though Matsushima reported that the adsorption of O₂ on polycrystalline Rh was not fully dissociative at 120 K,²³ and that of N₂ as end-on.^{13,15,24} As also suggested by Wang

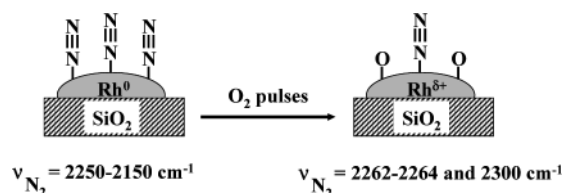


Figure 7. Schematic representation of the influence of O_2 addition on a Rh^0 crystallite whose exposed surface was saturated with chemisorbed N_2 species. For the sake of simplicity, N_2 chemisorbed species were assumed to adsorb via an end-on configuration and the dissociative adsorption of O_2 was only considered.

and Yates for an absorption contribution reported at 2276 cm^{-1} on a preoxidized $Rh(2.2)/Al_2O_3$ catalyst,¹³ it is likely that the back-donation from Rh to the orbitals of N_2 is significantly lowered by an electron-withdrawing oxygen ligand effect. In the case of Pt, Ozin et al. reported a shift as high as 60 cm^{-1} of the N_2 stretching frequency in an isolation comparative study of $Pt(N_2)$ and $Pt(O_2)(N_2)$ due to oxygen complexation.²⁵ In this sense, the results of the present study suggest that the vibrations observed above 2243 cm^{-1} are more likely attributable to N_2 chemisorbed on $Rh^{\delta+}$ surface atoms rather than Rh^0 as postulated by Wang and Yates or Worley and co-workers.^{13–15} The positive local deficient charge of these sites is induced by electron withdrawal of the oxygen chemisorbed on neighboring Rh surface atoms.

The original attribution of the band in the 2260 cm^{-1} region to N_2 chemisorbed on Rh^0 atoms,^{13–15} thus, deserves some discussions. First of all, it must be recalled that this assignation was drawn on Al_2O_3 -supported Rh catalysts. A support effect cannot account for the $40\text{--}50\text{ cm}^{-1}$ shift observed between the present study or that of Yates et al.¹² with those of Wang and Yates or Worley and co-workers.^{13–15} Yates et al.,¹² indeed, showed that a support effect can only be responsible for a 10 cm^{-1} shift when comparing a SiO_2 -supported Rh catalyst with an Al_2O_3 -supported one of comparable dispersion. Second, despite the fact that Wang and Yates or Worley and co-workers^{13–15} did not report on the Rh dispersion of their catalysts, it is very likely that their samples exhibited very high Rh dispersion, as the interaction of such a catalytic system with CO led to the formation of $Rh^I(CO)_2$ in great quantity.²⁶ Consequently, the band at $2256\text{--}2257\text{ cm}^{-1}$ attributed originally to N_2 chemisorbed on Rh^0 atoms^{13–15} might rather be assigned to N_2 chemisorbed on electron-deficient Rh clusters ($Rh^{\delta+}$ atoms) due to electron withdrawal from the oxygen atoms anchoring the Rh clusters onto the Al_2O_3 support. The assignation of the band at about 2260 cm^{-1} to N_2 chemisorbed on $Rh^{\delta+}$ atoms is further supported by recent DFT calculations reported by Citra and Andrews.²⁷

The attribution of the band at 2300 cm^{-1} is less problematic. An overall agreement has been reported to N_2 chemisorbed on $Rh^{\delta+}$ atoms.^{13–15} This highest frequency band might be assigned to the adsorption of N_2 on the smallest Rh clusters. The effect of electron withdrawal from both surface oxygen and oxygen-anchoring species on the resulting partial positive charge of the Rh atoms must, indeed, be the most pronounced for the smallest Rh clusters. As is the case for N_2 chemisorbed on Rh^0 , the wide absorption region related to N_2 chemisorbed on $Rh^{\delta+}$ centers might be ascribed to the heterogeneity of these sites.

Finally, this work, thus, enables us to delimit ranges of wavenumbers for which the adsorption of N_2 can be considered to occur on either Rh^0 or $Rh^{\delta+}$ centers for ν_{N_2} lower or higher than 2243 cm^{-1} , respectively.

5. Conclusions

The low-temperature adsorption of N_2 on Rh/SiO_2 samples of various particle-size distributions was followed by FTIR. The addition of O_2 pulses on Rh^0 surfaces saturated with chemisorbed N_2 allowed us to reassign stretching frequencies attributed originally to $N_2\text{--}Rh^0$ to $N_2\text{--}Rh^{\delta+}$. The formation of the latter oxidized Rh species is assumed to be induced by electron withdrawal from the adsorbed oxygen species on Rh surface centers neighboring those onto which N_2 species are chemisorbed. This concept might be extended to highly dispersed supported catalysts such as the Al_2O_3 -supported Rh catalysts studied by Wang and Yates or Worley and co-workers,^{13–15} for which the very small Rh clusters become electron-deficient due to electron withdrawal of the oxygen species anchoring these clusters onto the Al_2O_3 support. The present work, thus, enables us to delimit ranges of frequencies for which the adsorption of N_2 can be considered to occur on either Rh^0 or $Rh^{\delta+}$ centers for ν_{N_2} lower or higher than 2243 cm^{-1} , respectively.

This study also shows the superiority of the pulsed- O_2 method compared to oxidizing pretreatments of prereduced samples, for which it might not have been possible to reach the present conclusions.

Finally, the N_2 -FTIR experiments performed on the studied catalysts suggest a lattice plane-selectivity of N_2 adsorption on Rh metallic planes of different natures which, to our knowledge, has not been reported yet for Rh. Experiments are currently under progress to try to unravel the nature of the Rh^0 planes responsible for the different absorption contributions reported in the present study.

Acknowledgment. The Ministère de l'Enseignement Supérieur et de la Recherche supported the work of Ms. C. Fontaine-Gautrelet (grant 8449-2003). We thank Dr. P. Beaunier for her assistance in TEM measurements and P. Lavaud for technical support.

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