Infrared study of nitrogen monoxide adsorption on palladium ion-exchanged ZSM-5 catalysts

Claude Descorme [a], Patrick Gélin [a,1], Michel Primet [a] and Christine Lécuyer [b]

[a] *Laboratoire d'Application de la Chimie à l'Environnement, UMR 9977 CNRS, Université Claude Bernard Lyon I, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

[b] *GAZ DE FRANCE, Direction de la Recherche, CERSTA, 361, avenue du Président Wilson, PO Box 33, 93211 La Plaine St-Denis Cedex, France*

Received 24 February 1996; accepted 15 July 1996

The adsorption of NO at room temperature on a H-ZSM-5 catalyst exchanged with $Pd(NH_3)_4^{2+}$ complex and activated in oxygen at 773 K has been examined by FTIR spectroscopy. After the oxidizing treatment, the Pd tetrammine complex decomposed into Pd(II) ions and/or Pd(II) hydroxyl complexes dispersed in the zeolite channels. The subsequent adsorption of NO at room temperature led to the reduction of Pd(II) to Pd(I) entities, resulting in the formation and adsorption of NO_2 on H-ZSM-5. The Pd(I) entities were shown to adsorb NO and form mononitrosyl complexes dispersed in the zeolite porosity and characterized by a single infrared absorption band at 1881 cm^{-1}. The Pd(I) mononitrosyl complex was shown to reversibly coordinate water and NO_2 molecules. The resulting nitrosyl complex was characterized by a single NO vibration band at 1836 cm^{-1}.

Keywords: palladium; ZSM-5 zeolite; FTIR spectroscopy; NO adsorption; TPD

1. Introduction

The catalytic reduction of nitrogen oxides with C_2 and higher hydrocarbons in the presence of excess oxygen has been the subject of growing interest in the past few years because of the need for NO_x removal from automobile exhaust gases. In the mean time, only very few studies were concerned with the use of methane as a reductant for NO_x emissions in spite of the economic impact of methane widely used as a fuel for electrical facilities and stationary combustion engines [1–10]. Methane can also represent an alternative fuel for automotive vehicles. This points out the need for developing catalytic DeNOx processes involving methane as reducing agent. Palladium ion-exchanged zeolites, especially palladium ion-exchanged ZSM-5, have been reported recently to be active and selective in the catalytic reduction of NO by methane in the presence of large concentrations of oxygen [11,12]. Much effort is still necessary to clarify the state of adsorbed NO, the interaction of NO with palladium ions, the reaction mechanism for NO activation at the active centre and subsequent formation of nitrogen molecules. In this paper we report an infrared study of the adsorption of NO and NO_2 on the activated palladium-exchanged ZSM-5 catalyst.

2. Experimental

The Pd exchanged ZSM-5 catalyst was prepared by conventional ion-exchange of the starting ammonium exchanged ZSM-5 sample (CBV 5020, Si/Al ratio of 25, from PQ Zeolites BV) in an aqueous solution of tetrammine Pd(II) nitrate at 353 K for 24 h under moderate stirring. The amount of salt was calculated so as to introduce 0.5 wt% Pd into the final material. After exchange, the preparation was thoroughly washed with deionized water, filtered and dried at 393 K overnight. The Pd catalyst was finally activated in flowing oxygen from room temperature up to 773 K at a linear ramp of temperature (low rate) and subsequently purged at 773 K for 1 h under flowing helium before being cooled down to room temperature. The resulting material was referred to as Pd-H-ZSM-5 and its chemical composition determined by atomic absorption spectroscopy corresponded to the following formula: $Na_{0.09}H_{3.31}Pd_{0.27}Al_{3.93}Si_{92.07}O_{192}$. The starting ammonium exchanged ZSM-5 material was also activated in oxygen according to the same procedure as the Pd-H-ZSM-5 catalyst so as to obtain the H-ZSM-5 catalyst.

The IR studies of NO or NO_2 adsorption on the H-ZSM-5 support and on the Pd-H-ZSM-5 catalyst were performed using self-supported samples wafers (18 mm diameter, weight of 20–30 mg) introduced into a home made IR-cell allowing in situ studies at varying temperatures under controlled atmosphere [13]. The Pd-H-ZSM-5 sample was heated in situ in flowing oxygen from ambient temperature up to 773 K at a linear ramp rate of 10 K min^{-1} and purged in a helium flow at 773 K for 1 h before being cooled down to room temperature. The cell was subsequently connected to a UHV system allowing a base pressure as low as 10^{-8} Torr (1 Torr = (101 325/

[1] To whom correspondence should be addressed.

760) Pa) in order to be evacuated at 293 K before the introduction of NO or NO_2. The same experimental activation procedure was used for the IR studies of the support. The IR spectra were recorded at a resolution of 4 cm^{-1} on a FT-IR spectrometer Nicolet Magna 550. All the reported spectra have been obtained after subtracting the spectrum of the in situ activated sample in order to highlight the spectral changes resulting from the NO_x adsorption.

The quantitative measurement of NO adsorption on the Pd-H-ZSM-5 catalyst and the subsequent thermoprogrammed desorption (TPD) were performed by using a Balzers QMA 125 quadrupole mass spectrometer. These experiments were carried out in a U-shaped quartz reactor loaded with 0.12 g Pd catalyst bed. The Pd-H-ZSM-5 sample was pretreated in situ in flowing oxygen at 773 K with a linear ramp of temperature (low rate) and purged in He flow for 1 h before cooling to 298 K. The NO adsorption was achieved at 298 K by flowing the sample with helium and injecting in the flow five successive pulses of pure NO (each pulse corresponded to a gas volume of 0.255 cm^3 STP). After the last pulse of NO, the sample was further purged for 5 min in He flow at 298 K before subsequent heating up to 973 K at a linear ramp rate of 20 K min^{-1}. The desorbed species were continuously monitored as a function of time/temperature. The mass spectrometer was calibrated for NO, NO_2, N_2O, N_2 and O_2 gases. The amount of NO irreversibly adsorbed at 298 K was deduced from the NO pulses adsorption experiment and from the TPD profiles (by integrating the profiles of the N-containing gases).

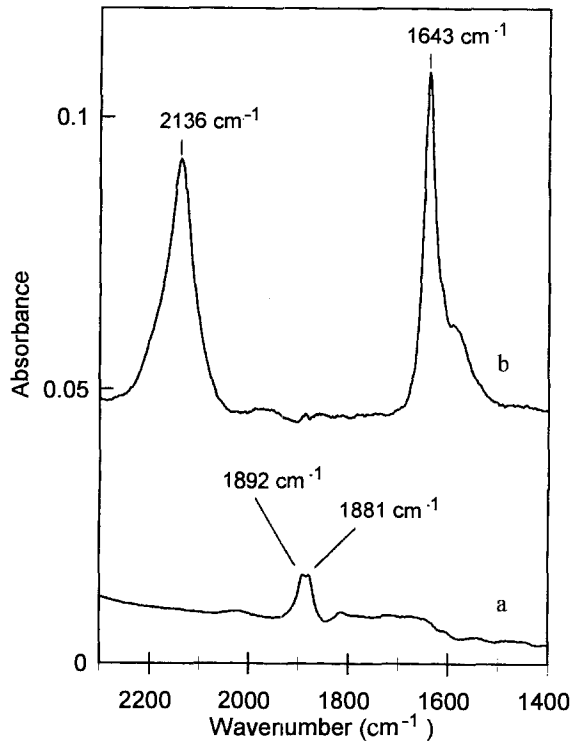

Fig. 1. IR spectra of NO (a) and NO_2 (b) adsorption onto H-ZSM-5 sample at room temperature. The spectra of the H-ZSM-5 sample under vacuum after activation and the gas phase have been subtracted. (a) $P_{NO} = 0.93$ Torr; (b) the amount of NO_2 introduced into the cell (1.5×10^{-4} mole per gram of zeolite) was totally adsorbed onto the sample.

3. Results and discussion

3.1. Adsorption of NO and NO_2 on H-ZSM-5

Fig. 1a shows the IR spectrum, in the NO region, of the adsorption of 0.93 Torr NO at room temperature onto the starting H-ZSM-5 material after standard activation at 773 K. A very weakly intense doublet is observed at 1892 and 1881 cm^{-1} ascribed to NO interacting with acidic hydroxyls of the zeolite through hydrogen bonding and forming NO^+ species. This interpretation agrees with the displacement of the two bands toward higher frequencies relatively to NO gas phase (1876 cm^{-1}). Indeed, it is well known that NO^+ is produced by partial removal of the electron density from the antibonding orbital of NO, therefore inducing an increase of the NO bond strength and consequently an increase of ν NO wavenumber. The small intensity of the NO bands is quite consistent with the very small amount of NO adsorbed on the zeolite at room temperature.

Fig. 1b shows the IR spectrum of the activated H-ZSM-5 sample contacted with NO_2 (1.5×10^{-4} mole per gram of catalyst). Two sharp features were observed at 2136 and 1643 cm^{-1}. Although not shown, the band at 3610 cm^{-1} characteristic of the acidic hydroxyls of the zeolite was partially depleted and a weakly intense and broad band around 3320 cm^{-1} was formed. These observations strongly suggest the formation of NO_2^+ species resulting from the hydrogen bonding between NO_2 and acidic hydroxyls of the zeolite. The interaction of NO_2 with acidic ZSM-5 hydroxyls is weak, as demonstrated by the total disappearance of the 2136 cm^{-1} band after mild heating under vacuum (323 K). On the contrary, the 1643 cm^{-1} band was almost not affected upon evacuation. This band could be tentatively ascribed to nitrate species resulting from the reaction of NO_2 with the zeolite framework.

3.2. Adsorption of NO on Pd-H-ZSM-5

Pd zeolite systems are known for their unusual property of stabilizing palladium in various oxidation states depending on the activation treatment and the zeolite structure [14–16]. Thus, when starting with a Y zeolite exchanged with the palladium(II) tetrammine complex, it is possible to obtain Pd^{3+}, Pd^{2+} and Pd^+ after an oxidizing treatment followed by evacuation in vacuo at 773 K. It must be pointed out that most of the palladium present in the Y zeolite (about 99%) retain the same oxidation state as the starting complex, i.e. 2+ [17]. After activating the fresh Pd exchanged H-ZSM-5 sample in

flowing oxygen at 773 K followed by evacuation under vacuum at 773 K, the IR spectrum reveals the disappearance of the weakly intense band at 1315 cm^{-1} characteristic of NH_3 ligands. This indicates the decomposition of the starting Pd(II) tetrammine complex with removal of NH_3 from the coordination sphere of Pd(II) ions. The Pd-H-ZSM-5 sample turns then to the beige pink colour observed for PdY systems and characteristic of the presence of palladium mostly in the 2+ oxidation state. Note that the absence of any ESR signal is also consistent with the presence of palladium in the 2+ oxidation state which is diamagnetic with a d^8 configuration. These results together with the absence of detectable PdO particles (by XRD and transmission electron microscopy) suggest that the original Pd(II) complex has simply decomposed into Pd(II) entities upon activation treatment. It is not clear if Pd(II) ions are isolated ions anchored to oxygen anions of the zeolite structure in crystallographic positions of the framework or form Pd(II) hydroxyl complexes. The latter hypothesis is preferred because, if present, water molecules are expected to be ionized by the strong electric field of the Pd cations and, owing to the very low Pd loading, only traces of water are necessary for the total formation of Pd(II) hydroxyl complexes. We propose therefore to denominate the decomposed Pd complex as $Pd(II)(OH)_x$ moieties, x being equal to 1 or 2.

Upon contacting the activated Pd-H-ZSM-5 sample with 0.12 Torr NO at 300 K, the IR spectrum is dominated by the appearance of three peaks at 2136, 1881 and 1840 cm^{-1} (fig. 2a), while the 3610 cm^{-1} band characteristic of the acidic hydroxyls of the zeolite structure is partially consumed. Clearly, the formation of the 2136 cm^{-1} band can be unambiguously ascribed to NO_2 interacting with acidic hydroxyls of the zeolite. The strong ν NO band at 1881 cm^{-1} as well as the shoulder at 1840 cm^{-1} are ascribed to NO adsorbed on Pd ions, because being absent when contacting the support with NO. Treatment under vacuum at 300 K does not affect the intensities of the three bands at 2136, 1881 and 1840 cm^{-1} (fig. 2b). The 2136 cm^{-1} band is totally removed upon evacuation at 323 K, confirming the presence of NO_2 weakly bound to the zeolite surface, in addition the intensity of the 1881 cm^{-1} band slightly decreases. The striking feature is that upon contacting the resulting sample with NO again, almost no formation of NO_2 could be detected while the intensity of the 1881 cm^{-1} band was restored. These results indicated that adsorbed NO_2 did not result from NO_2 present as impurities in the NO feed or obtained by reaction of NO with traces of oxygen but from a surface reaction between the activated Pd-H-ZSM-5 sample and nitrogen monoxide. A further confirmation of the surface reaction between Pd ions and NO was obtained by contacting the activated Pd sample with NO at low temperature. The sample was cooled to 223 K under vacuum before admitting 0.1 Torr NO. The 1881 cm^{-1} band partially formed and as the temperature

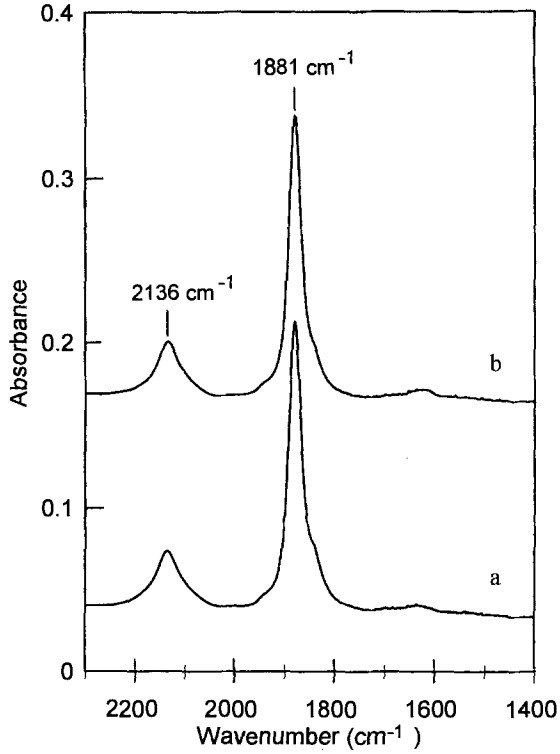

Fig. 2. IR spectral changes of the activated Pd-H-ZSM-5 sample upon contacting with 0.12 Torr NO at 300 K (a) and after subsequent vacuum treatment at 300 K for 10 min (b).

decreased new bands ascribed to NO physisorbed on the support are observed. The subsequent progressive warm up of the sample to ambient temperature under NO atmosphere led to the complete formation of the 1881 cm^{-1} band. It is concluded that the reaction of NO with the pretreated Pd-H-ZSM-5 sample is an activated process. The formation of NO_2 would therefore imply the partial reduction of Pd(II) ions to Pd(I) or Pd(0) entities. The existence of one single absorption band at 1881 cm^{-1} is ascribed to the formation of a mononitrosyl palladium complex, the origin of the shoulder at ca. 1840 cm^{-1} will be discussed later. The shift of the ν NO band with respect to gaseous NO (1876 cm^{-1}) will depend on two factors, (i) the electron donation from non-bonding NO orbitals to empty d-orbitals of Pd ions, (ii) the back donation from the Pd d-orbitals to the antibonding orbitals of NO. Therefore the position of the ν NO band is sensitive to the oxidation state of palladium: NO adsorbed onto metallic palladium gives rise to two main ν NO bands at 1740 and 1660 cm^{-1} [18] because of the strong donating effect of metal atoms in the particles, whereas NO adsorption onto Pd^{2+} ions leads to ν (NO) bands at 1865 and 1745 cm^{-1} [14]. As a consequence, the band at 1881 cm^{-1} must be attributed to NO adsorbed onto palladium species in an oxidized state, probably Pd(I) species because of the concomitant formation of NO_2. Based upon purely spectroscopic arguments, it is suggested that the reaction of NO with activated Pd-H-ZSM-5 catalyst leads to the reduction of Pd(II) to Pd(I)

ions and subsequent coordination of NO to Pd(I) entities to form mononitrosyl Pd(I) complexes.

In order to establish the stoichiometry of the reaction of NO with the exchanged palladium ions, the NO adsorption was measured quantitatively by flowing the sample with helium and injecting successive pulses of known volume of pure NO. NO is no longer adsorbed onto the Pd-containing sample after adsorption of 1.03 cm^3 STP of nitric monoxide. Such a volume corresponds to an irreversible adsorption of NO at 298 K. A ratio of 1.5 NO molecule per introduced Pd ion can be deduced from this experiment.

Then a TPD experiment was carried out in flowing helium by raising linearly the temperature from ambient temperature up to 923 K with a ramp of 20 K min^{-1}. The TPD profiles of desorbed N_2O, NO_2 and NO are shown in fig. 3. At low temperature (below 600 K), a large amount of NO_2 is desorbed with a maximum desorption rate at ca. 485 K. In the same time smaller amounts of NO were also identified in the thermodesorbed products whereas traces of N_2O were also detected. At higher temperature only NO is detected as desorbed molecule. From a quantitative point of view, the amounts of desorbed NO_2, NO and N_2O per palladium ion are found to be equal to 0.58, 0.82 and 0.06 respectively leading to an atomic nitrogen to palladium ratio of 1.52. Such a value is in good agreement with the NO/Pd ratio (1.50) deduced from the NO adsorption experiment.

From spectroscopic and quantitative measurements of the NO adsorption on activated Pd-H-ZSM-5, several successive reactions can be postulated to explain the reduction of Pd(II) into Pd(I) and coordination of NO by Pd(I) entities to form Pd(I) mononitrosyl complexes dispersed in the zeolitic channels of the ZSM-5 structure.

With the assumption of the presence of one hydroxyl group in the coordination sphere of Pd^{2+} ions, the adsorption-reaction of NO onto the Pd-H-ZSM-5 zeolite could be represented as follows:

$$2Pd(II)(OH)(O_z) + NO \rightarrow 2Pd(I)O_z + NO_2 + H_2O$$

$$2Pd(I)(O_z) + 2NO \rightarrow 2Pd(I)(NO)(O_z)$$

with $O_z = [Al\text{–}O\text{–}Si]^-$.

3.3. *Adsorption of other molecules onto the Pd–NO complex*

3.3.1. *Water adsorption*

Fig. 4 shows the IR spectra resulting from the addition of increasing amounts of water vapour to the Pd(I)(NO) complex supported on H-ZSM-5 zeolite. After contacting the Pd-H-ZSM-5 sample with a 0.07 Torr NO pressure (fig. 4a), the IR spectrum is characterized by two peaks at 2136 and 1881 cm^{-1} previously attributed to NO_2 adsorbed on acidic hydroxyl groups and Pd(I)(NO) complexes respectively. The 1836 cm^{-1} band evidenced in fig. 2 is very small, appearing only as a shoulder. As a small amount of water (2.5×10^{-4} mole per gram of hydrated catalyst, i.e. about 1/5 of the amount adsorbed at saturation) was added to the Pd(I)(NO) complex, the sample being still in contact with 0.03 Torr NO, we can observe the development of broad and intense bands in the ν OH region accompanied by the strong decrease of the 3610 cm^{-1} band. This result is characteristic of water molecules interacting with acidic hydroxyls of the H-ZSM-5 support. In addition, the intensity of the band at 2136 cm^{-1} has decreased, indicating a partial removal of NO_2 from acidic hydroxyls due to the competitive adsorption with

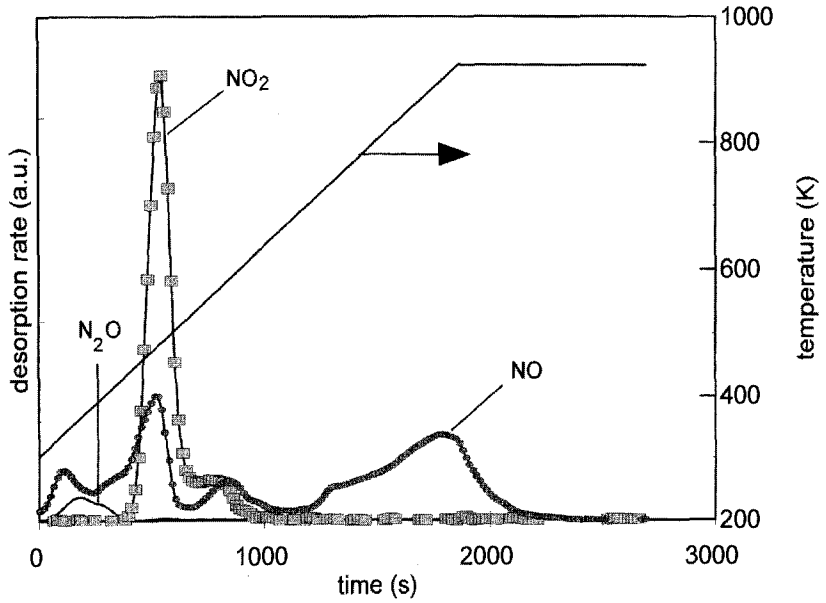

Fig. 3. Profiles of temperature programmed desorption of NO over Pd-H-ZSM-5 in flowing helium.

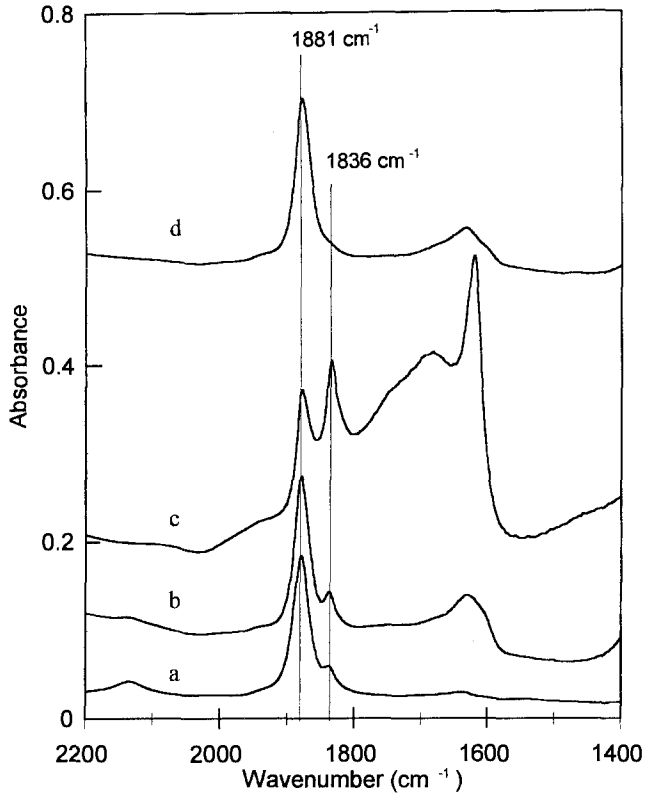

Fig. 4. IR spectral changes of the activated Pd-H-ZSM-5 sample upon addition at 298 K of NO and NO : H_2O mixtures: (a) after activation and subsequent introduction of 0.07 Torr NO, (b) after addition of water vapour (2.5×10^{-4} mole per gram of catalyst); $P_{NO} = 0.035$ Torr, (c) in the presence of a mixture of 0.15 Torr NO and 0.3 Torr water vapour, (d) after treatment under vacuum at 298 K for 10 min.

water molecules. The shoulder at 1836 cm^{-1} has developed into a band distinct from the 1881 cm^{-1} band whose intensity has increased too. Further addition of water so that a $NO/H_2O = 1 : 2$ mixture (0.45 Torr pressure) is admitted onto the Pd-H-ZSM-5 sample at room temperature leads to the strong increase of the 1836 cm^{-1} band intensity at the expense of the 1881 cm^{-1} one (fig. 4c). Evacuation of the sample under vacuum at room temperature regenerates the 1881 cm^{-1} band intensity while the 1836 cm^{-1} band goes down (fig. 4d). These results suggest that the band at 1836 cm^{-1} is due to a similar mononitrosyl complex where at least one lattice oxide ion acting as a ligand has been replaced by a water molecule. Similar effects have been observed on monovalent dicarbonyl complexes of rhodium encaged in Y zeolite cavities [19]. Depending on the hydration degree of the zeolite, different carbonyl complexes were identified and associated with distinct IR bands. Pd(I) mononitrosyl complexes supported on H-ZSM-5 might be considered as Lewis acid sites, therefore being able to coordinate a water molecule in addition to lattice oxide ions. This is thought to induce an increase in the electron backdonation from the Pd d-orbitals to the antibonding orbitals of coordinated NO, thus resulting in a decrease of the ν NO vibration toward lower frequencies compared to the Pd(I) mononitrosyl.

3.3.2. *Nitrogen dioxide adsorption*

The adsorption of NO_2 on the Pd(I)(NO) complex formed in the H-ZSM-5 matrix has been also examined. The Pd(I)(NO) complex supported on H-ZSM-5 was obtained as previously described by reacting 0.12 Torr NO at 298 K with activated H-ZSM-5. The IR spectrum obtained after subsequent evacuation at 323 K for 20 min is shown in fig. 5a. The further introduction of NO_2 (equilibrium pressure = 10^{-2} Torr) at 298 K is accompanied by the appearance of the 2136 cm^{-1} band characteristic of NO_2 interacting with acidic hydroxyls of the H-ZSM-5 structure (fig. 5b). Simultaneously, the band at 1880 cm^{-1} decreases and the band at 1836 cm^{-1} forms together with a strong band at 1643 cm^{-1}. Upon evacuation at 323 K (fig. 5c), the 2136 cm^{-1} band is totally depleted, indicating the total removal of weakly adsorbed NO_2. In the mean time, the 1836 cm^{-1} band is also removed, suggesting that its formation is related to the adsorption of NO_2 on the Pd nitrosyl complex, occupying a vacant coordination site of the Pd ion, in the same way as water molecules do. As upon water adsorption, the formation of the 1836 cm^{-1} band can be attribu-

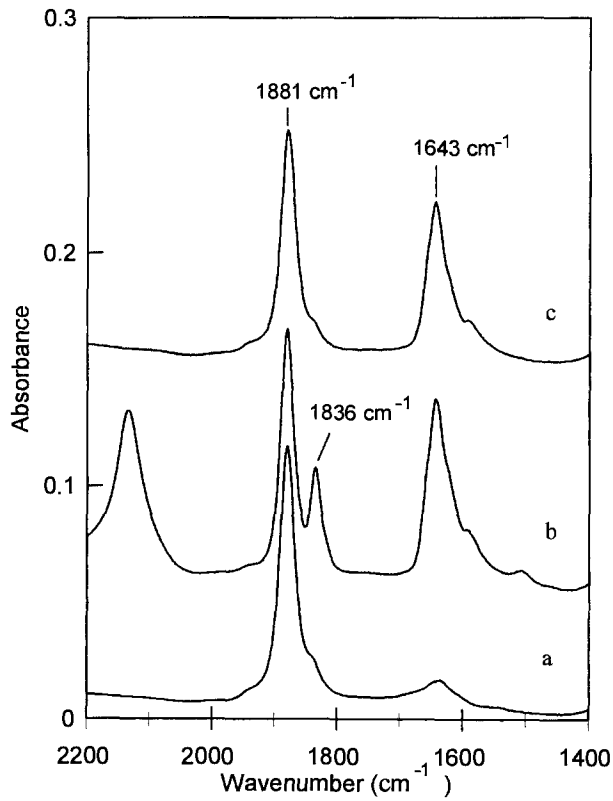

Fig. 5. IR spectral changes of Pd nitrosyl complexes formed on H-ZSM-5 upon NO_2 adsorption: (a) after reacting the activated Pd-H-ZSM-5 sample with NO at 298 K ($P_{NO} = 0.12$ Torr) and subsequent evacuation at 323 K for 20 min, (b) then, after contact of 1.0×10^{-2} Torr NO_2 at 290 K, (c) and subsequent treatment in vacuo at 323 K for 30 min.

ted to the coordination of the NO_2 molecule to a vacant site of the Pd–NO complex. The shift of the ν NO band from 1881 to 1836 cm^{-1} must be due to an increase in the backdonation in the π^* NO orbitals because of adsorption of an electron donor molecule in the coordination sphere of palladium ions.

4. Concluding remarks

Adsorption of NO at room temperature onto Pd(II) ions exchanged into H-ZSM-5 zeolite leads to the reduction of Pd ions from the 2+ to the 1+ oxidation state. In the mean time NO is oxidized into NO_2 which is weakly bonded to acidic hydroxyl groups and more firmly adsorbed onto other sites of the zeolitic matrix. A subsequent adsorption of NO leads to the formation of mononitrosyl palladium complex detected by a ν NO band at 1881 cm^{-1}.

Quantitative mass spectrometry measurements of NO adsorption confirm the formation of Pd(I) species since the consumed NO molecules/Pd ions ratio is close to 1.5. A similar N/Pd ratio value is also observed during desorption experiments which also evidence the presence of NO_2 in the desorbed products.

The Pd(I)–NO complex encaged in the zeolitic matrix is able to coordinate other molecules like H_2O and NO_2. The addition of water and nitrogen dioxide is evidenced by the formation of a new ν NO band at ca. 1836 cm^{-1} which develops at the expense of the 1881 cm^{-1} one.

Acknowledgement

The authors are very grateful to ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie) for financial support.

References

[1] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L31.
[2] K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, Chem. Lett. (1993) 229.
[3] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.
[4] Y. Li, P.J. Battavio and J.N. Armor, J. Catal. 142 (1993) 561.
[5] Y. Li and J.N. Armor, Appl. Catal. B 3 (1993) 55.
[6] Y. Li and J.N. Armor, J. Catal. 145 (1994) 1.
[7] T. Tabata, M. Kokitsu and O. Okada, Catal. Lett. 25 (1994) 393.
[8] E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73.
[9] R. Burch and S. Scire, Appl. Catal. B 3 (1994) 295.
[10] F. Witzel, G.A. Sill and W.K. Hall, J. Catal. 149 (1994) 229.
[11] A. Fakche, B. Pommier, E. Garbowski, M. Primet and C. Lécuyer, French Patent Appl. 9308006, Gaz de France (1993).
[12] C. Descorme, P. Gélin, M. Primet, C. Lécuyer and J. St-Just, *Zeolites: a Refined Tool for Designing Catalyic Sites*, Studies in Surface Science and Catalysis, Vol. 97 (Elsevier, Amsterdam, 1995) p. 287.
[13] N. Echoufi and P. Gélin, J. Chem. Soc. Faraday Trans. 88 (1992) 1067.
[14] M. Che, J.F. Dutel, P. Gallezot and M. Primet, J. Phys. Chem. 80 (1976) 2371.
[15] M. Primet and Y. Ben Taarit, J. Phys. Chem. 81 (1977) 1317.
[16] J.S. Yu, J.M. Comets and L. Kevan, J. Chem. Soc. Faraday Trans. 89 (1993) 4397.
[17] C. Naccache, M. Primet and M.V. Mathieu, Adv. Chem. Ser. 121 (1973) 266.
[18] S. Moriki, Y. Inoue and J. Yasumori, J. Chem. Soc. Faraday Trans. I 78 (1982) 171.
[19] F. Lefebvre, P. Gélin, C. Naccache and Y. Ben Taarit, *Proc. VIth Int. Zeolite Conf.*, eds. D. Olson and A. Bisio (Butterworths, Guildford, 1984) p. 435.