

FTIR study of the interaction of NO₂ and propene with Pt/BaCl₂/SiO₂

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Abstract

The interactions between NO₂ and BaCl₂/SiO₂ and Pt/BaCl₂/SiO₂ and the subsequent reaction of propene with the NO₂ derived surface and bulk complexes have been studied using FTIR. Barium nitrate species are generated in both cases along with surface nitrosyl species on Pt. Heating in vacuum increased the degree of crystallinity of the nitrate in the absence of Pt or in cases where Pt–Ba interactions were absent but led to partial decomposition for samples where Pt was in intimate contact with Ba. Heat treatment in the presence of propene accelerated the rate of nitrate decomposition for Pt/BaCl₂/SiO₂ and this could be further enhanced using a prerduced sample. Propene does not appear to interact directly with the nitrate but acts by removing oxygen from the metal surface. No evidence was obtained to indicate a role of organo-nitro species in the process. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: FTIR; NO₂; Pt/BaCl₂/SiO₂; Propene

1. Introduction

Control of car exhaust emissions currently involves engine operation in a small window close to stoichiometry where so called three-way catalysts can simultaneously convert NO, CO and unburned hydrocarbons to N₂, CO₂ and H₂O [1,2]. Although this system is efficient in terms of emission control, the restriction of operating close to stoichiometry imposes a penalty in terms of high fuel consumption. Engines may be operated efficiently at much higher

(ca. 20:1) air/fuel ratios leading to improved fuel consumption but in the presence of excess oxidant, current three way catalysts are ineffective for NO_x reduction. For these lean burn conditions, many alternative types of catalyst have been considered including copper-based materials [3–5] with Cu-ZSM-5 been the most widely studied [6–10]. These alternatives offer limited efficiency in terms of NO_x conversion and in particular offer poor stability, high light off temperatures and high sensitivity to SO₂. A recently proposed alternative [11–13] is to store the NO_x on the catalysts surface during lean burn operation and using engine management control, offer brief, regular intermissions in which the engine runs under stoichiometric con-

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ditions. This results in the release of the NO_x which can be reduced efficiently under these conditions by standard three-way catalyst components.

At the moment, little is known about the mechanistic details of the sequence of reactions and a detailed knowledge resulting from such studies may allow some of the key problems associated with the system to be addressed. Infrared spectroscopy has already been applied to studies of catalyst surfaces operating under lean burn operating conditions [5,10] and this approach is currently being extended to the area of NO_x storage and reduction (NSR) catalysts.

In our first report on these materials, a simplified model system has been adopted. Silica rather than alumina has been chosen as support thus avoiding the complication of NO_x adsorption on the support surface and barium chloride rather than oxide has been selected. It is known that adsorption of atmospheric CO_2 takes place readily on basic oxides, such as those of the alkaline earth metals [14]. This process leads to the formation of carbonates, which are only eliminated after extreme thermal treatments. These species present active IR modes in the same range of the spectrum where many NO_x surface complexes give absorption bands. In order to avoid interferences and simplify the handling of samples, materials based on BaCl_2 have been used in the present study.

2. Experimental

The 5% $\text{BaCl}_2/\text{SiO}_2$ sample was prepared by impregnation of Aerosil 200 with an aqueous solution of $\text{BaCl}_2 \cdot \text{H}_2\text{O}$. The excess solvent was removed by heating under continuous stirring. The powder obtained was dried overnight at 368 K, and subsequently calcined in a flow of air at 673 K for 4 h.

The 1% $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst was obtained by impregnation, in excess solvent, of the $\text{BaCl}_2/\text{SiO}_2$ support with a aqueous solution of H_2PtCl_6 (Johnson Matthey). Once the excess

solvent was removed, the sample was dried overnight at 368 K, and stored without any further treatment. XRD experiments on the samples in their dried states were carried out in a Philips PW 1729 diffractometer, using CuK_α radiation. BET surface area measurements, on samples outgassed at 423 and 573 K, were performed using a Micromeritics 2205 Surface Area Analyser using Ar as adsorbate. The dispersion of Pt was measured for a sample reduced at 573 K in flowing H_2 , by introducing a succession of 0.323 μmol pulses of CO into the carrier gas, with the sample at 298 K, and measuring the proportion of consumed CO using a TCD detector fitted to a Perkin-Elmer Autosystem XL gas chromatograph.

FTIR spectra were recorded in the transmission mode over the range 4000–1000 cm^{-1} at 4 cm^{-1} resolution using a Perkin-Elmer 1750 fitted with MCT detector (dynamic experiments) or a 1720X fitted with TGS detector (static experiments). In all cases, the samples were pressed into 25 mm diameter, self-supporting discs of 75–85 mg, and 30 scans were accumulated to produce each spectrum. Background spectra of the solids prior to gas adsorption were taken and substrated from subsequently recorded spectra.

Static adsorption experiments were conducted in a IR cell connected to a conventional vacuum line. Before gas admission, the discs were pretreated in a flow ($100 \text{ cm}^3 \text{ min}^{-1}$) of dry air at 623 K for 30 min, or, alternatively, in a H_2 flow ($100 \text{ cm}^3 \text{ min}^{-1}$) at 573 K for 30 min. The samples were cooled to room temperature and outgassed until pressures less than $2 \cdot 10^{-2} \text{ N m}^{-2}$ were achieved. In some cases, analysis of the gas phase was conducted by FTIR, after condensation of the products into a low volume, long (10 cm) path length cell or by injection into a GC-MS.

For flow experiments, an experimental arrangement was used which comprised of a pc-controlled gas blender attached to a high temperature transmission IR cell. Before exposure to reactant gases, the sample discs were cal-

cined in situ at 623 K for 30 min in a flow of dry air ($75 \text{ cm}^3 \text{ min}^{-1}$). The catalysts were cooled to 573 K before being submitted to consecutive NO (165–180 mmol) and C_3H_6 (460–510 mmol) pulses in dry air. The propene was dosed under net reducing ($\lambda = 0.84$) conditions. Spectra were recorded at the treatment temperature.

Propene (99.99%), NO(4.84%)/ N_2 and synthetic air (R.G.) were used as supplied by BOC. NO_2 (BDH, 99.5%) was vacuum-distilled before use in order to remove NO impurities.

3. Results

3.1. Sample characterisation

The XRD pattern of the $\text{BaCl}_2/\text{SiO}_2$ sample after calcination at 673 K shows the presence of crystalline $\text{BaCl}_2 \cdot \text{H}_2\text{O}$, as indicated by characteristic peaks corresponding to d -spacings of 5.50, 3.06 and 2.41 Å, along with broad features due to the amorphous silica. BET surface areas for Pt containing samples outgassed at 423 and 573 K were 125 and $123 \text{ m}^2 \text{ g}^{-1}$, respectively. The dispersion of platinum in the sample after reduction at 573 K was 30% ($\text{CO}/\text{Pt} = 0.299$).

3.2. NO_2 adsorption

FTIR spectra of the $\text{BaCl}_2/\text{SiO}_2$ sample 10 min after exposure to NO_2 at increasing pressures are displayed in Fig. 1. This period has been taken as the equilibration time as changes in band intensities were observed during the first minutes after exposure to the gas. At low pressures of NO_2 , (Fig. 1a), the spectrum shows bands at 1680, 1627, 1425 and 1354 cm^{-1} , along with weaker peaks at 1809 and 1789 cm^{-1} . At higher gas pressures (Fig. 1f–g), additional bands at 1744, 1595, 1316 and a broad band at 1878 cm^{-1} became evident. Simultaneously, the low frequency broad bands shifted from 1425 to 1418 cm^{-1} , and from 1354 to

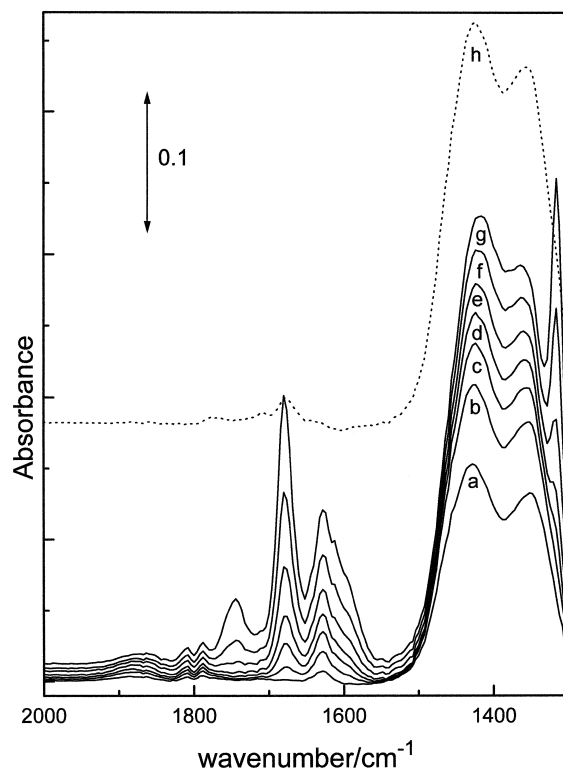


Fig. 1. FTIR spectra of $\text{BaCl}_2/\text{SiO}_2$ calcined at 623 K, 10 min after exposure to increasing pressures of NO_2 (a) 13, (b) 53, (c) 100, (d) 147, (e) 267, (f) 573 and (g) 933 N m^{-2}) and (h) after brief outgassing at room temperature.

1360 cm^{-1} . After extended periods of exposure, bands at 1744, 1627 and 1595 cm^{-1} diminished slightly while the rest of the features detected in this spectral range were significantly enhanced in intensity.

After brief evacuation at room temperature, (Fig. 1h), bands at 1878, 1809, 1789, 1626, 1592 and 1316 cm^{-1} were removed completely, while those at 1744 and 1680 cm^{-1} were attenuated. Lower wavenumber bands were less affected by the vacuum treatment and only a slight loss of intensity at around 1410 cm^{-1} could be detected. This behaviour, along with the evolution of the absorbance with NO_2 pressure (Fig. 2), strongly suggests that bands at 1360 and 1418 cm^{-1} correspond to the same chemical species. Although the peak at 1316 cm^{-1} is partly obscured by other overlapping bands, its intensity is affected in a similar man-

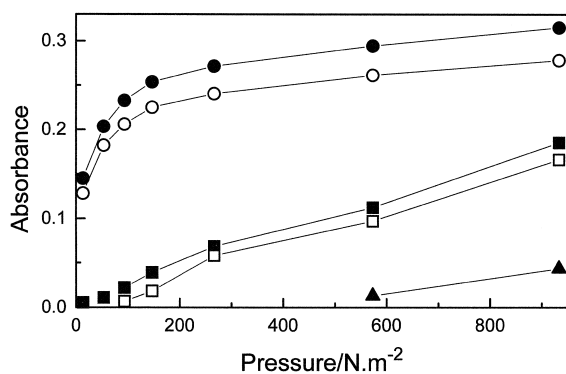


Fig. 2. Plots of band intensity as a function of NO_2 pressure admitted; (■) 1680 cm^{-1} , (□) 1316 cm^{-1} , (●) 1418 cm^{-1} , (○) 1360 cm^{-1} and (▲) 1744 cm^{-1} for $\text{BaCl}_2/\text{SiO}_2$.

ner by changes in the NO_2 pressure as the band at 1680 cm^{-1} . Both bands can be assigned to a single species.

Spectra of the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst recorded 10 min after the admission of increasing pressures of NO_2 are shown in Fig. 3. Most of the features detected for the $\text{BaCl}_2/\text{SiO}_2$ sample are also observed after the incorporation of the precious metal, without any significant variations in frequency or response to changes in gas phase pressure. However, peaks at 1809 and 1789 cm^{-1} are no longer discernible due to overlap with a strong band at $1840\text{--}1790\text{ cm}^{-1}$ and another weak, broad band is detected at 2162 cm^{-1} . The intensity of this last feature increased with increasing gas pressures and with contact time. However, the band at ca. 1830 cm^{-1} shows a more complex behaviour characterised by frequency shifts. This fact, along with the asymmetric lineshape of the peak suggest that it consists of several components. Immediately after admission of a small amount of gas the maximum is at 1796 cm^{-1} , while after an increase in NO_2 pressure, the most intense contribution appears at 1824 cm^{-1} . Finally, for the highest NO_2 pressures studied here, the maximum is centred at 1839 cm^{-1} . Although outgassing at room temperature does not significantly modify this band, the same treatment fully removed the species giving the band at 2162 cm^{-1} .

The temporal evolution of the spectrum of the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst after the admission of a fixed amount of NO_2 is displayed in Fig. 4. As indicated above for the Pt free sample, bands at 1744 , 1626 and 1592 cm^{-1} diminish as a function of exposure time, while those at 1680 , 1418 , 1360 and 1316 cm^{-1} simultaneously gain intensity. On the other hand, while the feature at 1839 cm^{-1} decreased in intensity, the band at 2162 cm^{-1} increased slightly. This clearly indicates that some of species detected are slowly converted into more stable adsorbed complexes.

3.3. Thermal stability of adsorbed species

When the $\text{BaCl}_2/\text{SiO}_2$ sample is heated briefly in static vacuum at 563 K , the form of the spectrum (Fig. 5) changes dramatically. Both low frequency bands sharpen markedly revealing an additional feature indicated by a shoulder

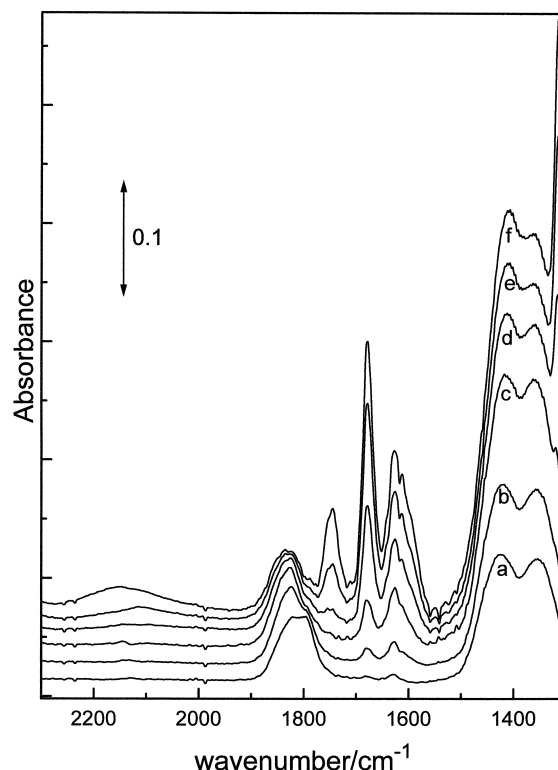


Fig. 3. FTIR spectra of $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ calcined at 623 K , 10 min after exposure to increasing pressures of NO_2 . (a) 13, (b) 67, (c) 187, (d) 240, (e) 547 and (f) 973 N m^{-2} .

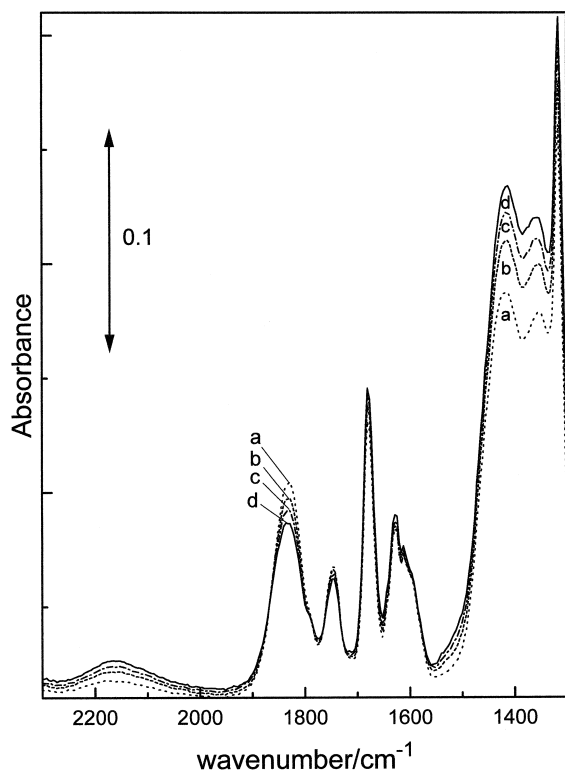


Fig. 4. FTIR spectra of Pt/BaCl₂/SiO₂ calcined at 623 K, exposed to 773 N m⁻² of NO₂ (a) immediately after admission and after (b) 5, (c) 11 and (d) 25-min contact.

at 1460 cm⁻¹. This is accompanied by a change in their relative intensity and by a shift to 1368 cm⁻¹ of the low frequency band. A weak feature at 1775 and a broad band around 2400 cm⁻¹ (not shown) also appear in the spectra. These changes to the spectra are identical to those observed when a physical mixture of Pt/SiO₂ and BaCl₂/SiO₂ is treated in the same manner. Similar modifications to the spectrum could also be induced by heating the BaCl₂/SiO₂ in the presence of propene. After prolonged treatment in the presence of alkene, an additional poorly resolved band appears at ca. 1700 cm⁻¹. At this stage, the gas phase spectrum shows bands characteristic of NO₂, and less well defined features due to N₂O and NO.

The Pt/BaCl₂/SiO₂ catalyst (Fig. 6) behaves in a very different manner when heated at

563 K following room temperature evacuation. This treatment results in an initially rapid reduction in intensity of bands at 1418 and 1368 cm⁻¹ but requires about 20 min to approach completion. After this period, the overall intensity losses are very slight in this range of the spectrum. A poorly resolved band at around 1620 cm⁻¹ is observed in addition to the detection of NO₂ in the gas phase, and trace amounts of N₂O and NO.

Different behaviour is observed when the Pt/BaCl₂/SiO₂ catalyst, previously contacted with NO₂, is submitted to C₃H₆ at 563 K. The spectra obtained following such treatment for a sample prereduced in H₂ at 573 K are displayed in Fig. 7. Initially, the adsorption of C₃H₆ at room temperature results in the formation of species exhibiting a band at 1635 cm⁻¹ (Fig. 7b), which was also detected for BaCl₂/SiO₂

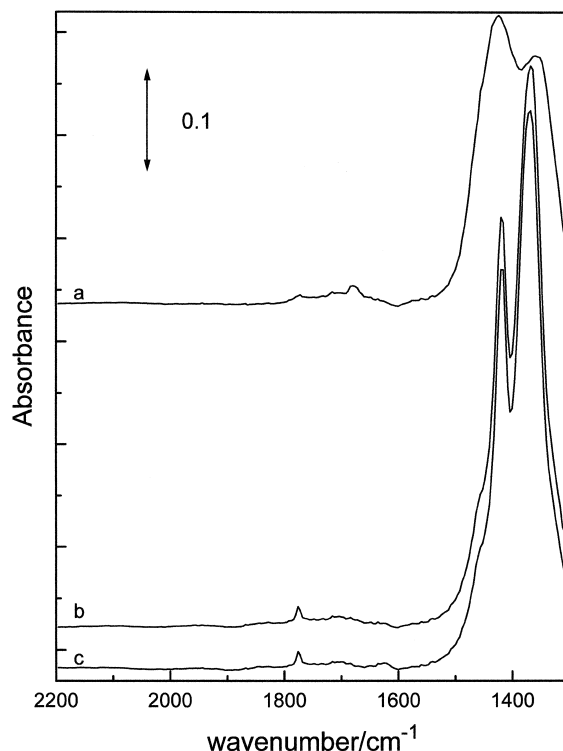


Fig. 5. FTIR spectra of BaCl₂/SiO₂ calcined at 623 K, (a) exposed to NO₂ (533 N m⁻², 20 min), evacuated at room temperature and (b) heated at 563 K for 3, and (c) 6 min.

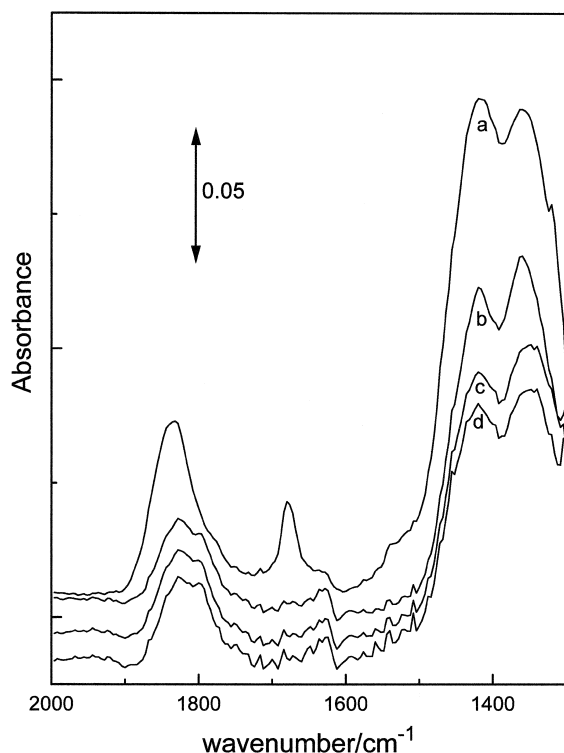


Fig. 6. FTIR spectra of Pt/BaCl₂/SiO₂ calcinated at 623 K, exposed to NO₂ (773 N m⁻², 25 min), (a) evacuated at room temperature and heated at 563 K for (b) 5, (c) 10 and (d) 20 min.

after exposure to the alkene. After 20 min contact with the hydrocarbon, (Fig. 7c) the peak at 1839 cm⁻¹ diminishes in intensity and a simultaneous increase in the band at 1635 cm⁻¹ is observed. An additional weak band at 2130 cm⁻¹ is detected. Heat treatment at 563 K in the presence of C₃H₆ (Fig. 7d), almost completely removes the species giving the band at 1839 cm⁻¹ and a new peak at 1697 cm⁻¹ is detected. After a few minutes at high temperature both low frequency bands lose intensity and become sharper. However, these features are progressively eliminated by continued treatment under these conditions. At this stage, additional absorption bands at 2176 and 2071–68 cm⁻¹ became discernible. In contrast, when the Pt/BaCl₂/SiO₂ sample is pretreated in air, a peak at 2125 cm⁻¹, along with a weak, broad band at 2195 cm⁻¹ appear in the spectra following this treatment. Apart from these differences,

modifications to the spectrum took place more gradually for the calcined sample. The gas phase spectrum indicates the presence of N₂O for both reduced and calcined samples while mass spectroscopic analysis of the gas phase detected various isomers of chloropropane and chloropropanone when the preoxidised catalyst was heated in the presence of propene.

The influence of these treatments on the low frequency bands is summarised in Fig. 8. The species formed on BaCl₂/SiO₂ are affected to a lesser extent than those on Pt/BaCl₂/SiO₂ by high temperature treatment, either in vacuum or under propene. However the behaviour of the physical mixture of Pt/SiO₂ and BaCl₂/SiO₂ is more akin to the platinum free sample. Although heating the Pt/BaCl₂/SiO₂ under hy-

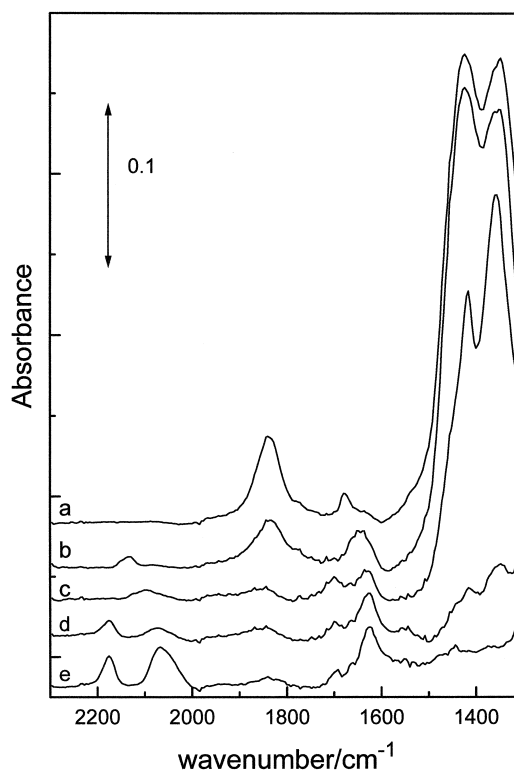


Fig. 7. FTIR spectra of Pt/BaCl₂/SiO₂ reduced at 623 K in H₂, exposed to NO₂ (347 N m⁻², 30 min), (a) evacuated at room temperature, contacted with propene (720 N m⁻²) for (b) 1, (c) 20 min and heated at 563 K for (d) 2, (e) 5 and (f) 17 min.

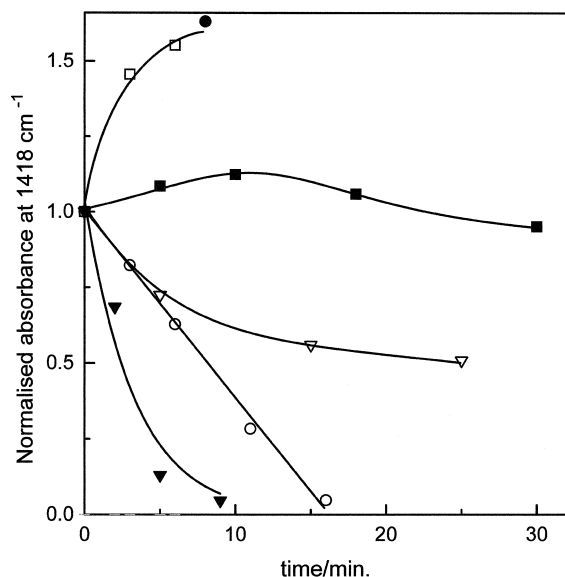


Fig. 8. Plots of the normalised intensity at 1418 cm^{-1} as function of the treatment time at 563 K for (□) $\text{BaCl}_2/\text{SiO}_2$ in static vacuum, (●) $\text{Pt}/\text{SiO}_2 + \text{BaCl}_2/\text{SiO}_2$ in static vacuum, (■) $\text{BaCl}_2/\text{SiO}_2$ under propene, (▽) calcined $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ in static vacuum, (○) calcined $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ under propene and (▼) reduced $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ under propene.

drocarbon always results in the removal of the species giving the band at 1418 cm^{-1} , the process occurs more rapidly for a prereduced sample.

3.4. NO and C_3H_6 pulses in air

In order to gain further insight into the interactions of propene with the adsorbed NO_x under conditions more akin to those present in exhaust systems, additional experiments were performed under flow conditions. Spectra obtained after submitting the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst to successive pulses of NO and C_3H_6 at 573 K using air as diluent, are shown in Fig. 9. Pulses of NO in air lead to the appearance of a broad band envelope with maxima at about 1406 and 1360 cm^{-1} . The intensities of these bands increase with the number of pulses, and decay slightly in the intervening period between pulses. In spite of the small differences in frequency and relative intensity, it would appear that these bands correspond with those at 1418 and 1360 cm^{-1}

observed by adsorption of NO_2 at room temperature, and indicate the formation of the same species. The species responsible for these bands are significantly attenuated after the admission of a single pulse of propene (Fig. 9f) which also leads to the appearance of a broad band centred at ca. 1569 cm^{-1} . This new feature was enhanced by a second pulse of C_3H_6 but remained essentially constant after further pulses. The broad maxima replacing the $1406/1360\text{ cm}^{-1}$ doublet was still present after several propene pulses.

3.5. Band assignments

The gas phase spectrum of NO_2 shows two intense bands at 1626 and 1595 cm^{-1} , corresponding to the R and P branches, respectively, of the asymmetric $\nu(\text{NO}_2)$ stretching vibration [15,16]. As the gas phase has not been sub-

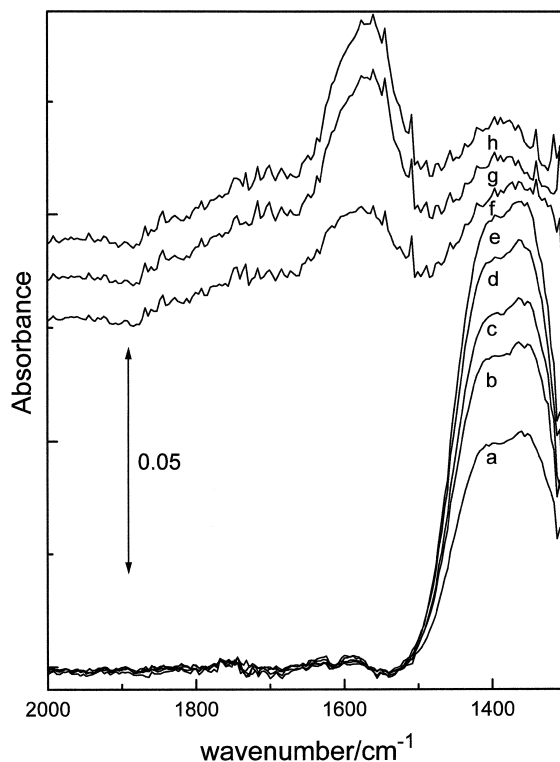


Fig. 9. FTIR spectra of $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ calcined at 623 K after consecutive pulses of NO in air, (a)–(e), and propene, (f)–(h) at 573 K .

strated from the spectra reported here, bands appearing at those frequencies can be related to unadsorbed NO_2 . Similarly, the band at 1744 cm^{-1} may be attributed to the asymmetric stretching mode of N_2O_4 . This dimer exists in equilibrium with NO_2 and represents an important component of the gas phase at moderate temperatures [15,16]. However, this alone cannot account for the total absorbance at 1744 cm^{-1} as indicated by performing a gas phase subtraction. This dimer has been detected by EEL spectroscopy after multilayer adsorption of NO_2 on $\text{Ru}(001)$ surfaces [17]. Although this system and the experimental conditions are quite dissimilar from those used here, the observed frequencies coincide and the presence of N_2O_4 interacting with the surface of the samples under study would appear feasible.

Bands at 1809 and 1789 cm^{-1} are also present in spectra of the gas phase after contact with the barium-containing surfaces. However, these are absent in the spectrum of the purified NO_2 and do not correspond to any fundamental vibration of any nitrogen oxides [15,16]. Formation of a nitrogen oxyhalide by reaction of NO_2 with the chlorinated surfaces is plausible. The $\nu(\text{NO})$ mode of the ClNO molecule is detected by IR spectroscopy at 1800 cm^{-1} [16]. The other active vibrations of this molecule appear below 1000 cm^{-1} and would be undetected in the present study. Bands at 1809 and 1789 cm^{-1} , are therefore assigned to the R and P branches, respectively, of the nitrosyl stretching vibration of nitrogen oxychloride.

Nitrates of different symmetries are known to be formed following NO_2 adsorption on metal oxides [18] and supported metal catalysts [19,20]. In the case of surface coordinated NO_3^- , bands in the ranges 1650 – 1500 cm^{-1} and 1300 – 1170 cm^{-1} are expected. Metal nitrates, on the other hand, usually show bands at lower frequencies than the analogous coordination compounds, with the symmetric stretching mode appearing about 1050 cm^{-1} , and the asymmetric stretching mode in the 1530 – 1200 cm^{-1} range [21]. This data would suggest an assign-

ment of the bands observed at 1418 and 1360 cm^{-1} to the formation of $\text{Ba}(\text{NO}_3)_2$, with the latter consistent with the reported value of 1354 cm^{-1} for $\nu_a(\text{NO}_2)$ [11,21]. Formation of any type of barium nitrite is unlikely under the conditions of the current study. Moreover, the most important spectral features of such species are centred around 1260 cm^{-1} [22,23]. This range of vibrations is not discernible due to the high background absorption of the SiO_2 , but the envelope of these bands should be detected at frequencies above 1300 cm^{-1} . Further evidence for the formation of $\text{Ba}(\text{NO}_3)_2$ can be obtained from the spectra displayed in Fig. 10. The spectrum of the pure nitrate, characteristic of a monodentate group, resembles that of the $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ after NO_2 adsorption. Furthermore, there are only slight differences in frequency, when compared with the spectrum of the $\text{BaCl}_2/\text{SiO}_2$ sample exposed to NO_2 and heated at 563 K .

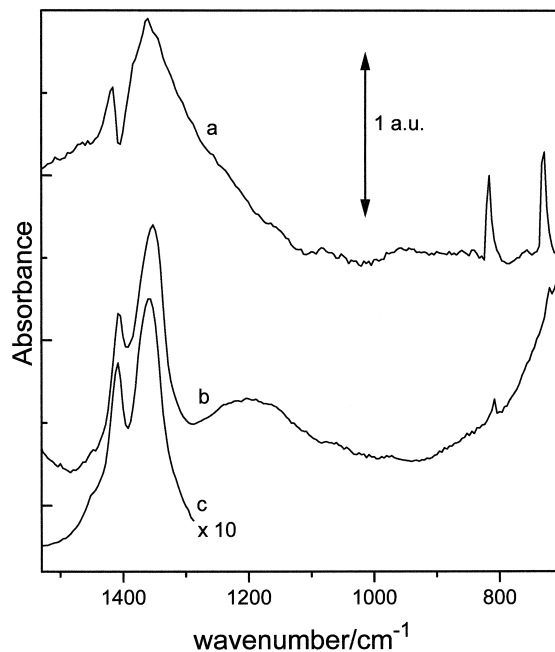
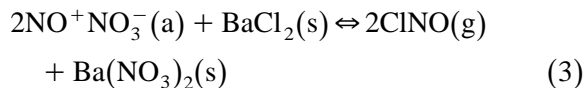
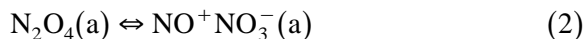


Fig. 10. FTIR spectra of (a) $\text{Ba}(\text{NO}_3)_2$ diluted in KBr ; (b) $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ calcined at 623 K and exposed to NO_2 (680 N m^{-2} , 85 min); and (c) $\text{BaCl}_2/\text{SiO}_2$ calcined at 623 K , exposed to NO_2 (533 N m^{-2} , 20 min), evacuated at room temperature and heated at 563 K for 6 min (as Fig. 5c).

The above data allows the interaction of NO_2 with the BaCl_2 surfaces to be explained according to the following reaction scheme

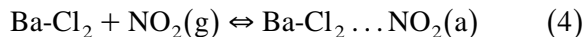


Equilibria (1) and (2) have been reported for NO_2 adsorption on oxides and rhodium catalysts, leading to the generation of nitrates and nitrosonium complexes [18–20]. In addition, the observed intensity decrease at 1744 cm^{-1} and the simultaneous increase in the low frequency bands during prolonged exposure to NO_2 , is consistent with these reactions. Although the monohydrate form of the chloride was detected by XRD, the anhydrous form has been considered in the reaction (3) as it may be assumed that the water of crystallisation is removed from the supported barium chloride under the pretreatment conditions used.

The nitrate formed initially at room temperature probably exists in a rather disordered state, as deduced from the broad nature of the IR bands (Fig. 5a). Additionally, interactions with other adsorbed species is likely, as suggested by the slight loss of intensity on outgassing at room temperature. The annealing of $\text{BaCl}_2/\text{SiO}_2$ at 563 K in a reducing atmosphere (under vacuum or propene) yields spectra with well-defined bands, analogous to those of the crystalline $\text{Ba}(\text{NO}_3)_2$. In the case of the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$, this phase transformation is not so clearly observed (Fig. 6), although in this case, heating leads to a partial decomposition of the nitrate.

The surface complexes giving bands at 1680 and 1316 cm^{-1} cannot be attributed to any fundamental vibration of nitrates because, as mentioned above, they give bands at lower wavenumbers. Furthermore, the conditions required for the formation of such species suggests that they correspond to an oxychlorinated nitrogen compound. One feasible assignment might be to adsorbed ClNO_2 . In the gas phase

this molecule gives bands at 1685 and 1319 cm^{-1} , due to the asymmetric and symmetric NO_2 stretching modes, respectively [16,21]. The spectra obtained may be interpreted in terms of equilibrium (4):



The bonding between chlorine and nitrogen is likely to be weak, consistent with the ease of removal of these species by outgassing at room temperature.

Bands in the region $1840\text{--}1795\text{ cm}^{-1}$ are attributed to nitrogenated species adsorbed on platinum, as these are absent in spectra of the $\text{BaCl}_2/\text{SiO}_2$ sample. Adsorption of NO_2 on Pt (111) at temperatures around 100 K results in the formation of a $\mu\text{-N,O-nitrito}$ surface complex. At higher temperatures, adsorption is dissociative and the surface of the metal becomes covered by NO and O atoms [24]. IR spectra of supported platinum catalysts in the presence of NO_2 , show bands in the $1850\text{--}1750\text{ cm}^{-1}$ region [19,20,25,26] assigned to linearly bound NO on platinum particles, which, in accordance with single crystal results, result from dissociation of NO_2 at room temperature. Although most studies have dealt with platinum in a reduced state, there are reports on the coadsorption of oxygen and NO [25,27]. These investigations have shown that the frequency of the N-O stretching mode increases with oxygen coverage. This has been explained in terms of changes in the Pt-NO bond, induced by removal of electronic density by the oxygen. In the case of the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst, the band frequency does not vary significantly with the pretreatment condition, suggesting that the state of the surface after exposure to NO_2 is similar for both reduced and calcined samples. The formation of any type of platinum oxide after admission of nitrogen dioxide can be ruled out on the basis of single crystal studies [27], therefore the most feasible explanation would be that the platinum is partly reduced after calcination due to the thermal decomposition of the oxide.

NO_2 adsorption leads to the formation of NO coadsorbed with oxygen on sites of different coordination number and terrace size, characterised by bands at 1839, 1824 and 1795 cm^{-1} . In line with previous remarks, the highest wavenumber band may correspond to NO on a surface with a high coverage of O atoms. Modifications in band shape with the amount of NO_2 admitted can be related to the extent of dissociative/associative adsorption. Previous studies using $\text{Rh}/\text{Al}_2\text{O}_3$ indicate that band broadening and a shift from 1910 to 1934 cm^{-1} accompany the formation of $\text{NO}^+ \text{NO}_3^-$ from a surface layer of dissociatively adsorbed NO_2 when NO_2 pressure is increased [19,20]. Changes in intensity at 1839 cm^{-1} with contact time, suggests that species adsorbed on the metal surface contribute to the formation of $\text{Ba}(\text{NO}_3)_2$ and ClNO_2 . This process may take place by spillover of NO and oxygen or by transport through the gas phase.

The band at 2162 cm^{-1} is ascribed to a NO^+ complex, as these ions are the only nitrogen oxides that present $\nu(\text{NO})$ shifted to such high frequencies [16,18,28]. As mentioned above, formation of these species can take place following reaction (2). Decomposition of ClNO provides an alternative route for the generation of nitrosonium ions. This nitrogen oxyhalide is relatively unstable [28], and its rupture may be Pt catalysed. Similarly, the broad, weak band at 1880 cm^{-1} found in the spectra of $\text{BaCl}_2/\text{SiO}_2$ may be ascribed to nitrosonium ions, which are known to give bands in this region when coordinated to certain surface cations [29]. However, the presence of adsorbed NO, either as an impurity or produced by interaction with the solid, cannot be ruled out.

The adsorption of propene on both samples studied, independent of the pretreatment used, leads to the formation of a species giving an IR band at 1635 cm^{-1} . Bands in the range $1635\text{--}1600\text{ cm}^{-1}$ has been detected after alkene adsorption on several metal oxides and assigned to the $\nu(\text{C}=\text{C})$ of the hydrocarbon coordinated to surface cations with a formal charge greater or

equal to +2 [30]. In the case of the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$, this peak is progressively replaced during heating by bands at 1627 and 1697 cm^{-1} . The first of these features is very likely due to the bending mode of adsorbed water on silica, a product of oxidation of the hydrocarbon. This process would also explain the formation of small amounts of CO, as detected by IR bands indicative of linearly bound CO on Pt surfaces. For the calcined sample, the adsorption take place on oxidised sites or at surfaces where adsorbed oxygen exists, as deduced by the band at 2125 cm^{-1} [31]. A similar band at 2130 cm^{-1} is observed in the spectrum of the prerduced sample after several minutes contact with propene. This, along with the decrease in band intensity at 1839 cm^{-1} , indicates that some oxidation of the alkene occurs on the platinum surface even at room temperature. The dissociation of the NO_2 would provide the oxygen source for such a reaction. When the sample is exposed to C_3H_6 at 563 K, the CO detected is bound to metallic platinum, as deduced from bands at $2071\text{--}68\text{ cm}^{-1}$ [31]. The slight variation in the frequency is probably related to the co-adsorption of other species, such as hydrocarbon fragments, resulting in dilution of the adsorbed layer. On the other hand, the species responsible for the band at 1697 cm^{-1} may correspond to a nitrogenated complex, as these are detected for samples pretreated with NO_2 . Nitric oxide adsorbed on platinum gives bands in this range [25,26], but such an assignment seems unlikely given that a similar band at 1700 cm^{-1} is detected for $\text{BaCl}_2/\text{SiO}_2$ under the same conditions. Alternatively, this band may correspond to the adsorption of a nitrogenated organic molecule although the frequency is appreciably higher than the characteristic bands of organo-nitro and nitrite compounds [32–34]. Finally, adsorbed organic carbonyls have been detected during NO_x reduction by hydrocarbons on various catalysts [5,32–35]. Acrolein, which is a known intermediate in propene oxidation, gives a band at 1693 cm^{-1} when adsorbed on silica [35] and it would

seem reasonable to ascribe the feature at 1697 cm^{-1} to $\nu(\text{C}=\text{O})$ of adsorbed acrolein.

The band at 2179 cm^{-1} observed for Pt/BaCl₂/SiO₂ (Fig. 7e,f) may indicate the formation of isocyanate species. These species are readily formed by reaction of NO or NO₂ with hydrocarbons or CO on various supported metal catalysts [5,19,20,32–37]. Although the frequency corresponds closely with that reported for NCO on unsupported Pt [38], these species are normally rapidly transferred from the metal to the support surface [37]. Although it is known that spillover of NCO takes place less readily for SiO₂ supports [36,37], at the temperature of the current study it is expected that NCO should migrate to the silica, resulting in its detection by an IR band at ca. 2310 cm^{-1} [36,37]. The alternative would be that NCO is stabilised at Ba²⁺ sites after migration from Pt. In general, negatively charged species exhibit a lower $\nu_a(\text{NCO})$ than neutral NCO species and the band appears at ca. 2210 cm^{-1} for MgO [37] as an example of NCO adsorbed on an alkaline earth cation. If this band assignment to Ba–NCO is correct, then the formation of this species as opposed to the formation of Si–NCO gives evidence for the proximity of Ba and Pt within the catalyst, making the Pt/Ba/SiO₂ system a useful model for the NSR catalyst. Further support for the close proximity of Pt and Ba is given by the different behaviour of the nitrate species as indicated by the 1418 cm^{-1} band for the Pt/Ba/SiO₂ sample and the physical mixture of Pt/SiO₂ and BaCl₂/SiO₂ when treated under vacuum (Fig. 8).

In accordance with the literature a possible assignment for the 1569 cm^{-1} band detected under flow conditions for Pt/BaCl₂/SiO₂ may be to the $\nu(\text{NO}_2)$ mode of adsorbed organo nitro molecules [33,34]. However, bands around 3000 cm^{-1} , due to the C–H stretching modes of the organic skeleton [30] were not detected. Additionally, and in contrast with the behaviour of this species as indicated by this band, organo nitro complexes are unstable under oxygen at high temperature [33,34]. It is unlikely that this

band indicates organo nitro species and instead indicates surface complexes formed by interaction of the partially oxidised alkene with BaO. Surface carboxylate complexes such as acetates and acrylates have been detected during NO_x reduction with alkenes [32,39] and barium acetate gives two bands at 1557 and 1412 cm^{-1} due to the asymmetric and symmetric stretch of the COO – group [21]. The lower frequency component would be masked by the ca. 1400 cm^{-1} maximum, not fully removed following NO_x and subsequent propene pulses. This assignment is consistent with the detection of such species under oxidising conditions which exist between introducing pulses of propene.

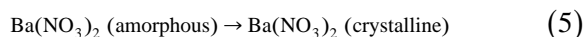
4. Discussion

Pt/SiO₂ catalysts are reported to be active for NO_x reduction by propene under excess oxygen conditions [40]. The first step of the reaction is believed to be oxidation of nitric oxide to NO₂ [33,34] and the reaction may reach its thermodynamic conversion limit over supported platinum catalysts [41]. The activity of various catalysts in NO₂ formation have been related to their De–NO_x performance [42].

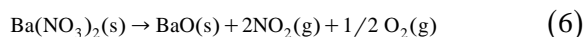
The next stage in the NO_x reduction mechanism implies reaction of NO₂ with the alkene [33,34]. It has been proposed that the products of this process are organo-nitro and nitrite compounds. These undergo further reaction yielding N₂, N₂O, H₂O and CO_x by a series of metal catalysed steps, although with limited NO_x conversion levels. By incorporating a NO_x storage component, additional reaction pathways become available resulting in improved NO_x reduction, by making use of the more efficient conversion under rich and stoichiometric conditions [11]. NO₂ interaction with the storage component yields nitrate type species, which are stable under oxidative conditions, but are decomposed under stoichiometric or reducing conditions. Details of the interaction of the nitrates with the alkene are not fully established, but it

is believed that some kind of NO_x species are released. These nitrogen oxides are subsequently reduced by hydrocarbons and CO to N_2 and N_2O on the platinum surface.

In the current study, the Pt/ BaCl_2 / SiO_2 catalyst has been found to be active for the oxidation of nitric oxide, as NO_2 is detected during NO pulses in air at 573 K at concentrations above those in the corresponding homogeneous reaction although neither reaction reaches equilibrium conversion [41]. As mentioned above, interaction of NO_2 with the BaCl_2 component leads to the formation of barium nitrate. Experiments involving NO_2 adsorption under static conditions for BaCl_2 / SiO_2 sample reveal that initially, this compound is in a rather disordered state, most likely corresponding to a mainly surface phase. However, after a brief period at 563 K, the nitrate undergoes the following phase transition



Many metal nitrates decompose before melting [28] which, in the case of barium nitrate, is transformed at 970 K into the corresponding oxide according [43] to the equation

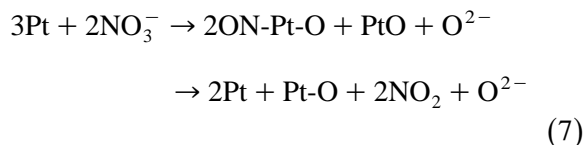


It is expected that at lower temperatures, a significant amount of NO_2 and O_2 would remain in equilibrium with the solid. However, if these gases are eliminated from the local environment, a shift of reaction (6) would lead to the complete decomposition of the nitrate at moderate temperatures. These processes would explain the behaviour of the nitrates detected for the BaCl_2 / SiO_2 sample. When this material is heated in vacuum, the $\text{Ba}(\text{NO}_3)_2$ increases in crystallinity but remains unchanged once the equilibrium is attained. In the presence of a reactive molecule, which taking into account the nature of the gases generated in (6) should be reducing, the amount of nitrate transformed may be increased. This appears to be the case when the BaCl_2 / SiO_2 sample is heated under propene, since both O_2 and NO_2 are susceptible to interaction with the alkene at 563 K. The

detection of a weak band due to an organic carbonyl as opposed to an organo nitrate type species and the absence of any apparent reduction in NO_2 concentration in the gas phase, may indicate that propene is reacting predominantly with O_2 . These processes most likely occur in the gas phase rather than being catalysed reactions. These assumptions are in agreement with the data in Fig. 8 where the increase in absorbance due to conversion to the crystalline phase is compensated by their partial decomposition, when the nitrates on BaCl_2 / SiO_2 are exposed to C_3H_6 at 563 K. On the other hand, the small quantities of NO and N_2O found after these treatments are very likely released during the decomposition of $\text{Ba}(\text{NO}_3)_2$.

In the case of Pt/ BaCl_2 / SiO_2 , the nitrates exhibit different behaviour consistent with the expectation that the noble metal component should offer alternate routes during nitrate decomposition. The phase transformation in (5) is not clearly observed, although some sharpening of the bands at 1418 and 1360 cm^{-1} is detected initially during heat treatments. This suggests the possibility of additional reactions competing with or hindering the crystallisation process. More rapid gas exchange between the nitrate and its immediate surroundings (6), might hinder the phase transformation. As the ordering of a solid implies the existence of fixed lattice positions, and this condition is unlikely to be met by a material undergoing continuous reorganisation, this assumption appears reasonable. The evolution of the spectra of NO_2 in contact with Pt/ BaCl_2 / SiO_2 as a function of time (Fig. 4) suggest that NO_2 initially adsorbed on platinum is depleted by migration to the barium component with the generation of nitrates. A similar influence of the precious metal during the NO_x storage process has been found for other NSR catalysts [11]. Additionally, results in Fig. 8, indicate the importance of platinum in the extent to which nitrate decomposition takes place during heat treatment in vacuum. In contrast, physical mixtures of Pt/ SiO_2 and BaCl_2 / SiO_2 behave like platinum-free samples.

It is possible that decomposition of the NO_3^- ion takes place at the interface between the barium component and the noble metal leading to release of NO_2 and most likely to formation of a surface oxygen layer on the metal surface, in accordance with the scheme:



This process, involving the accumulation of surface oxygen, would hinder the progress of nitrate decomposition in the absence of a reducing gas such as propene and would be enhanced by increasing the amount of Pt^0 as indicated by experiments conducted using a reduced $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ sample (Fig. 8).

When the $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst is heated in the presence of propene, the $\text{Ba}(\text{NO}_3)_2$ is totally eliminated with simultaneous formation of other adsorbed species. In the case of the calcined sample, reduction of residual oxidised platinum by the hydrocarbon may generate complete and partial oxidation products. For the catalyst pretreated in hydrogen, some alkene oxidation is also expected as oxygen is released by decomposition of the nitrate or by dissociative adsorption of NO_2 on the metal. This leads to adsorption of carbon monoxide on the metal, along with R-CO species and H_2O on the support. Although there are no indications of the formation of nitrogenated organic compounds, NCO species were detected using the platinum sample. These surface complexes have been suggested as intermediates in NO_x reduction by hydrocarbons and CO [33,34]. In the presence of propene, NO_2 is not observed, but N_2O is detected in the gas phase following extended treatment using the prerduced or calcined $\text{Pt}/\text{BaCl}_2/\text{SiO}_2$ catalyst. This suggests that the hydrocarbon reacts readily on the metal surface with any nitrogen oxide. Any nitrogenated organic intermediate, if formed, must be rapidly transformed, for example, into iso-

cyanate species which might subsequently yield CO , N_2O and probably N_2 as final products [33,34].

There is no evidence for direct reaction of propene with the barium nitrate under static conditions, but rather, a platinum catalysed reduction of the previously stored NO_2 . Dynamic experiments show that the interaction of C_3H_6 with the nitrates lead to the removal of the stored NO_2 under slightly rich conditions. Simultaneous partial and complete oxidation of the hydrocarbon takes place as indicated by the detection of surface carboxylates and gas phase CO_2 . This confirms that the model catalysts used in this study are effective in the storage and reduction of NO_x allowing conclusions obtained in this study to be extended to more complex NSR systems. Under excess oxygen conditions and in the presence of SO_2 , other reactions pathways become available and any mechanism of NO_x abatement on NSR catalysts, should include additional steps accounting for all the intermediates. In situ FTIR experiments are currently being carried out to gain further insight into these aspects.

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References

- [1] K.C. Taylor, *Catalysis—Science and Technology*, J.R. Anderson, M. Boudart (Eds.), Vol. 5, Springer, Berlin, 1984, p. 121.
- [2] B. Harrison, M. Wyatt, K.G. Gough, *Specialist periodical reports—catalysis*, R. Soc. Chem. London 5 (1982) 127.
- [3] H. Hosose, H. Yahiro, N. Mizuno, M. Iwamoto, *Chem. Lett.* 1859 (1991).
- [4] G. Centi, S. Perathoner, *Appl. Catal. A* 132 (1995) 179.
- [5] J.A. Anderson, C. Marquez Alvarez, M.J. Lopez-Muñoz, I. Rodriguez Ramos, A. Guerrero Ruiz, *Appl. Catal. B* 14 (1997) 189–202.
- [6] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, S. Kagawa, *J. Phys. Chem.* 95 (1991) 3727.
- [7] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, M. Iwamoto, *Appl. Catal.* 70 (1991) L1.

- [8] J. Valyon, W.K. Hall, *J. Phys. Chem.* 97 (1991) 1204.
- [9] R.H.H. Smits, Y. Iwasawa, *Appl. Catal. B* 6 (1995) L201.
- [10] N.W. Hayes, R.W. Joyner, E.S. Shpiro, *Appl. Catal. B* 8 (1996) 343.
- [11] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kashahara, *Catal. Today* 27 (1996) 63.
- [12] S. Matsumoto, *Catal. Surveys Jpn.* 1 (1997) 111.
- [13] M.V. Twigg, *Plat. Metals Rev.* 41 (1997) 76.
- [14] J.A. Anderson, C.H. Rochester, *J. Chem. Soc., Faraday Trans. 1* 82 (1986) 1911.
- [15] R.E. Nightingale, A.R. Downie, D.L. Rotenberg, B. Crawford Jr., R.A. Ogg Jr., *J. Phys. Chem.* 61 (1954) 1047.
- [16] J. Laane, J.R. Ohlsen, *Progress in Inorganic Chemistry*, V(27), in: Lippard (Ed.), 1980.
- [17] U. Schwalke, J.E. Parmeter, W.H. Weinberg, *J. Chem. Phys.* 84 (1986) 4036.
- [18] D.V. Pozdnyakov, V.N. Fillimonov, *Kinet. Katal.* 14 (1973) 655.
- [19] J.A. Anderson, G.J. Millar, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 86 (1990) 571.
- [20] J.A. Anderson, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 87 (1991) 1485.
- [21] S.D. Ross, *Inorganic Infrared and Raman Spectra*, McGraw-Hill, Maidenhead, London, 1972.
- [22] D.L. Wood, *J. Chem. Phys.* 75 (1981) 4809.
- [23] O.P. Lamba, H.D. Bist, *J. Phys. Chem. Solids* 44 (1983) 445.
- [24] M.E. Bartram, R.G. Windham, B.E. Koel, *Surf. Sci.* 184 (1987) 57.
- [25] A. Ghorbel, M. Primet, *J. Chim. Phys.* 73 (1976) 89.
- [26] B.A. Morrow, R.A. McFarlane, L.E. Moran, *J. Phys. Chem.* 89 (1985) 77.
- [27] M.E. Bartram, B.E. Koel, E.A. Carter, *Surf. Sci.* 219 (1989) 467.
- [28] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., Wiley-Interscience, New York, 1980.
- [29] M.C. Kung, H.H. Kung, *Catal. Rev.-Sci. Eng.* 27 (1985) 425.
- [30] A.A. Davydov, *Infrared spectroscopy of surface species on the surface of transition metal oxides*, in: C.H. Rochester (Ed.), 1990.
- [31] J.A. Anderson, *J. Chem. Soc., Faraday Trans.* 88 (1992) 1197.
- [32] T. Tabata, H. Ohtsuka, M. Kokitsu, O. Okada, *Bull. Chem. Soc. Jpn.* 68 (1995) 1905.
- [33] T. Tanaka, T. Okuhara, M. Misono, *Appl. Catal. B* 4 (1994) L1.
- [34] T. Okuhara, Y. Hasada, M. Misono, *Catal. Today* 35 (1997) 83.
- [35] J.A. Anderson, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 85 (1989) 1129.
- [36] J.A. Anderson, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 86 (1990) 3809.
- [37] F. Solymosi, L. Volgyesi, J. Raskó, *Z. Phys. Chem. N.F.* 120 (1980) 79.
- [38] J. Raskó, F. Solymosi, *J. Catal.* 71 (1981) 219.
- [39] J.A. Anderson, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 85 (1989) 1117.
- [40] G. Zhang, T. Yamaguchi, H. Kawakami, T. Suzuki, *Appl. Catal. B* 1 (1992) L15.
- [41] E. Xue, K. Seshan, J.G. Van Ommen, J.R.H. Ross, *Appl. Catal. B* 2 (1993) 183.
- [42] C. Yokoyama, M. Misono, *J. Catal.* 150 (1994) 9.
- [43] K. Machida, K. Yasuoka, K. Eguchi, H. Arai, *J. Chem. Soc. Chem. Commun.* 1165 (1990) .