

FTIR Spectroscopic Characterization of NO<sub>x</sub> Species Adsorbed on ZrO<sub>2</sub> and ZrO<sub>2</sub>–SO<sub>4</sub><sup>2–</sup>

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The nature of the NO<sub>x</sub> species produced during the adsorption of NO at room temperature and during its coadsorption with oxygen on pure and sulfated zirconia has been investigated by means of in situ FTIR spectroscopy. The adsorption of NO on both samples occurs through disproportionation leading to the formation of nitrous acid; water molecules; nitro species; and anionic nitrosyls, NO<sup>–</sup>. A mechanism for the formation of these adsorption forms is proposed. The NO<sup>–</sup> species are stable on the surface of zirconia, whereas on the sulfated sample, they are readily oxidized by the SO<sub>4</sub><sup>2–</sup> groups. The process of NO disproportionation is favored by wet surfaces and occurs with participation of the tribridged (ZrO<sub>2</sub>) and terminal (ZrO<sub>2</sub>–SO<sub>4</sub><sup>2–</sup>) hydroxyl groups. Coadsorption of NO and O<sub>2</sub> on pure zirconia leads to the formation of various kinds of nitrate species. The presence of sulfate ions reduces the amount of surface nitrates and decreases their thermal stability. An analysis of the combination bands of the nitrate species shows that this spectral region can be used for structural identification of bidentate and bridged nitrates.

## Introduction

Recent reports have shown that transition metal oxides supported on zirconia and sulfated zirconia are promising for the selective catalytic reduction (SCR) of NO with NH<sub>3</sub><sup>1,2</sup> and hydrocarbons.<sup>2–8</sup> Delahay et al.<sup>5,6</sup> demonstrated that the promotion of Cu/ZrO<sub>2</sub> (an effective catalyst in the SCR of NO with decane) by sulfate ions widens the temperature range of selectivity toward dinitrogen. To understand the effect of sulfation in the mechanism of NO reduction, it is important to obtain information on the nature and stability of the NO<sub>x</sub> species adsorbed on the surface of pure and sulfated zirconia. Infrared (IR) spectroscopy is one of the most powerful tools for the in situ characterization of adsorbed NO<sub>x</sub> species on catalytic materials.<sup>9</sup> However, only a few studies<sup>9</sup> have appeared employing this technique for the identification of surface NO<sub>x</sub> species produced during the adsorption of NO and during its coadsorption with oxygen on pure and sulfated zirconia.

In general, the interaction of NO with the surface of zirconia results in the formation of small amounts of NO<sub>x</sub> surface compounds. Some authors<sup>10–12</sup> have reported that nitrosylic species cannot form on pure zirconia, whereas others<sup>13–15</sup> have observed coordination of NO to Zr<sup>4+</sup> sites. Mononitrosyl species have been found on sulfated zirconia.<sup>11</sup> The adsorption of NO on pure<sup>10–15</sup> and sulfated zirconia<sup>11</sup> at room temperature gives rise to bands in the nitrito–nitrate region. However, interpretations of the bands in this region are quite contradictory. A typical example is the band at 1180–1190 cm<sup>–1</sup>, which has been assigned to nitrite<sup>10,13,15</sup> or nitrate<sup>12</sup> species. Greater amounts of NO<sub>x</sub> species (mainly nitrates and nitrites) on ZrO<sub>2</sub> are observed when NO and O<sub>2</sub> are coadsorbed at room temperature.<sup>12,15</sup> In the identification of NO<sub>x</sub> species adsorbed on zirconia, the use of bands in the combination region can be helpful.<sup>12</sup> The adsorption of NO<sup>12</sup> and NO/O<sub>2</sub> coadsorption cause alterations in the hydroxyl groups of zirconia,<sup>12,15</sup> and formation of chelated or bridged species of the type (O<sub>2</sub>NO–H)<sup>0–</sup> has

been proposed.<sup>15</sup> To the best of our knowledge, no IR data on the coadsorption of NO and O<sub>2</sub> on sulfated zirconia are available.

In this study, FTIR spectroscopy has been used to identify and determine the thermal stability of surface NO<sub>x</sub> compounds on pure and sulfated zirconia. An attempt is made at understanding the processes leading to the formation of NO and NO/O<sub>2</sub> adsorption forms.

## Experimental Section

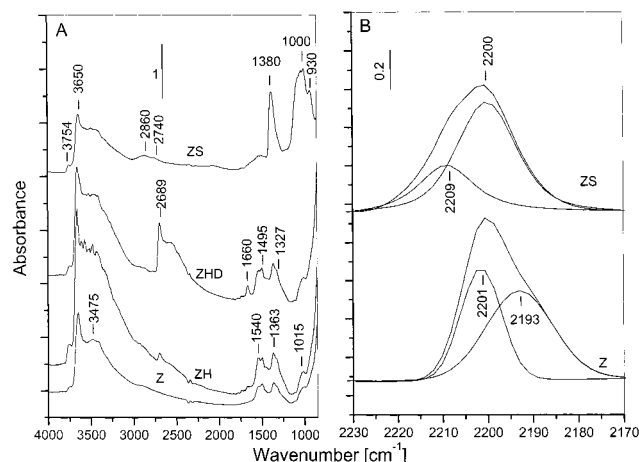
**Sample Preparation.** Zirconia was prepared by hydrolysis of ZrCl<sub>4</sub> (Merck, for synthesis) with a concentrated (25%) solution of ammonia. During the dissolution of ZrCl<sub>4</sub> in water (0.3 mol of ZrCl<sub>4</sub>/L) and addition of ammonia solution, the temperature was kept below 343 K. The precipitate was washed thoroughly with deionized water to remove the chloride ions, dried at 393 K for 12 h, and calcined for 4 h at 773 K. The BET surface area was 69 m<sup>2</sup>/g, and according to XRD, the substance was predominantly monoclinic (94%).

Sulfated zirconia was prepared by impregnation of the calcined material with a solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The nominal content of the sulfate ions was 3.8 wt %. The sulfation of zirconia led to an increase in the content of the tetragonal phase (10%). The BET surface area of this material was 83 m<sup>2</sup>/g.

**Surface Area Measurements and X-ray Diffraction.** The BET surface areas of the samples (dehydrated at 523 K) were measured by nitrogen adsorption at 77 K using a MONOSORP apparatus from Quantochrome. XRD analysis was performed on a Rigaku Miniflex diffractometer with Ni-filtered Cu Kα radiation under ambient conditions. The crystallographic phase composition was calculated using the method of Toraya et al.<sup>16</sup>

**Infrared Spectroscopy.** The FTIR spectra were recorded on a Bomem MB 102 FTIR (Hartman & Braun) spectrometer equipped with a liquid-nitrogen-cooled MCT detector at a resolution of 4 cm<sup>–1</sup> (128 scans). A specially designed IR cell allowed registration of the spectra at ambient temperature and catalyst activation at higher temperatures. The cell was connected to a vacuum/adsorption apparatus. Self-supporting disks (0.044 g/cm<sup>2</sup>) were used for the FTIR studies. These specimens

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**Figure 1.** FTIR spectra of the samples studied in the (A) OH-stretching region and (B) carbonyl region of CO (666.6 Pa) adsorbed at room temperature.

were activated by heating for 1 h in a vacuum at 673 K and in oxygen (133 kPa) at the same temperature, followed by evacuation for 1 h at room temperature (standard activation). Z denotes the zirconia sample that was subject to the standard activation procedure, whereas the designation ZS is used for the sulfated material. The partially deuterioxytated sample was obtained by introduction to the activated zirconia of water vapor (173.3 Pa) containing 50% deuterium, followed by evacuation at room temperature for 15 min and heating in a vacuum for 1 h at 623 K. The sample treated in this way is denoted ZHD. The hydroxylated sample of zirconia (notation ZH) was prepared by the same procedure using water vapor with normal isotopic content. The spectra of the activated samples (taken at ambient temperature) were used as a background reference. The spectra of the samples that were subject to treatment at elevated temperatures were recorded after the IR cell had been cooled to room temperature. All of the spectra presented (except those in Figure 1) were obtained by subtraction of the corresponding background reference.

The computer peak fittings were performed using the minimum number of peaks and fixed peak positions based on the original spectra. The sum of the squares of the deviations between the experimental points and fit values was less than  $10^{-4}$ .

The CO (99.95%, BOC, Ankara) used was passed through a trap cooled by liquid nitrogen before admission to the IR cell. The purity of NO gas was 99.9% (Air Products).

## Results and Discussion

### FTIR Spectra of the Activated Samples and Adsorbed CO.

Figure 1A shows the FTIR spectra of the pure and sulfated zirconia, which were subjected to different activation procedures. The spectrum of the Z sample in the OH-stretching region is similar to that reported by Guglielminotti<sup>17</sup> and is characterized by a weak band at 3750  $\text{cm}^{-1}$ , a sharp and strong band at 3650  $\text{cm}^{-1}$ , and a broad absorption with a maximum at 3475  $\text{cm}^{-1}$ . According to the literature data,<sup>18–20</sup> the former two bands are assigned to terminal (3750  $\text{cm}^{-1}$ ) and bridged OH groups (3650  $\text{cm}^{-1}$ ) coordinated to three Zr atoms. The broad band centered at 3475  $\text{cm}^{-1}$  is attributed to H-bonded tribridged hydroxyls.

Modification of zirconia with  $\text{SO}_4^{2-}$  ions (sample ZS) leads to a decrease in the population of bridged hydroxyl groups. This indicates that sulfate ions have replaced some of the three-coordinated OH groups.

The bands at 1540, 1495, 1363, 1327, and 1015  $\text{cm}^{-1}$  are due to bidentate carbonates.<sup>18,20</sup> Such residual surface species are often observed on zirconia and cannot be removed by high-temperature activation. The sharp band at 1380  $\text{cm}^{-1}$  and the broad, complex absorption with a maximum at 1000  $\text{cm}^{-1}$  observed on the sulfated sample are assigned to the split  $\nu_3$  mode, whereas the weaker band at 930  $\text{cm}^{-1}$  is attributed to the  $\nu_1$  mode of multidentate  $\text{SO}_4^{2-}$  groups coordinated to  $\text{Zr}^{4+}$  ions.<sup>21</sup> The magnitude of splitting (approximately 380  $\text{cm}^{-1}$ ) is typical of highly covalent sulfates.<sup>21</sup>

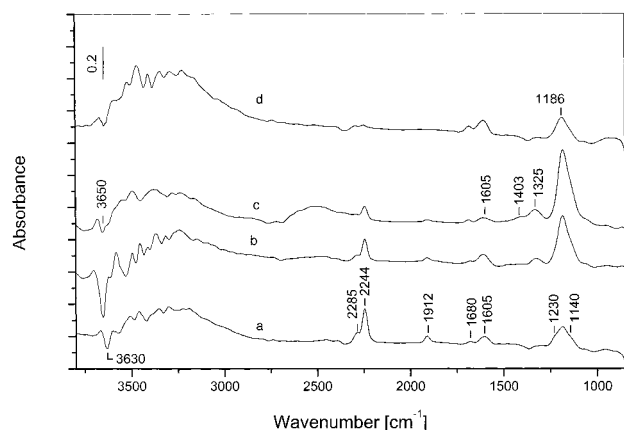
The partially deuterioxytated ZHD sample, in addition to the absorption in the OD region, exhibits a band at 1660  $\text{cm}^{-1}$ , which is probably due to a carboxylate structure. For the sulfated sample, the absorptions at 2860 and 2740  $\text{cm}^{-1}$  reveal the presence of formate species.<sup>20</sup> Most probably, the formate and carboxylate species are produced during the activation of the samples by interaction of CO and  $\text{CO}_2$ , respectively (formed as products of the decomposition of the residual carbonates), with the sample surface. Jung and Bell<sup>20</sup> showed that, in the formation of formate species from CO adsorbed at 523 K on zirconia, the surface hydroxyls are involved, and the extent of their participation depends on their acidity, being higher in the case of sulfated zirconia.<sup>21</sup> An alternative interpretation of the weak bands at 2860 and 2740  $\text{cm}^{-1}$  (observed only in the case of activated ZS sample) is to attribute them to first overtones of the band with a maximum at 1380  $\text{cm}^{-1}$  due to the  $\nu(\text{S}=\text{O})$  mode, which is not resolved in the fundamental region.

Figure 1B shows the IR spectra of adsorbed CO (666.6 Pa) at room temperature on the Z and ZS samples. Two overlapping bands centered at 2201 and 2193  $\text{cm}^{-1}$  are observed for the pure zirconia, which correspond to two types of  $\text{Zr}^{4+}$ –CO carbonyls.<sup>22</sup> For the sulfated sample, there is a high-frequency shift of both carbonyl bands: the band at 2193  $\text{cm}^{-1}$  detected on the pure zirconia is shifted to 2200  $\text{cm}^{-1}$  ( $\Delta\nu = 7 \text{ cm}^{-1}$ ), and the band at 2201  $\text{cm}^{-1}$  to 2209  $\text{cm}^{-1}$  ( $\Delta\nu = 8 \text{ cm}^{-1}$ ). This indicates that modification of the surface by sulfate ions causes an increase in the strength of the Lewis acid sites as a result of the presence of charge-withdrawing  $\text{SO}_4^{2-}$  groups.<sup>21,23</sup> It should be pointed out that, in the case of the sulfated sample, the total population of coordinatively unsaturated  $\text{Zr}^{4+}$  sites has decreased. Obviously, there are sulfate groups directly coordinated to the  $\text{Zr}^{4+}$  sites making them inaccessible for CO adsorption.

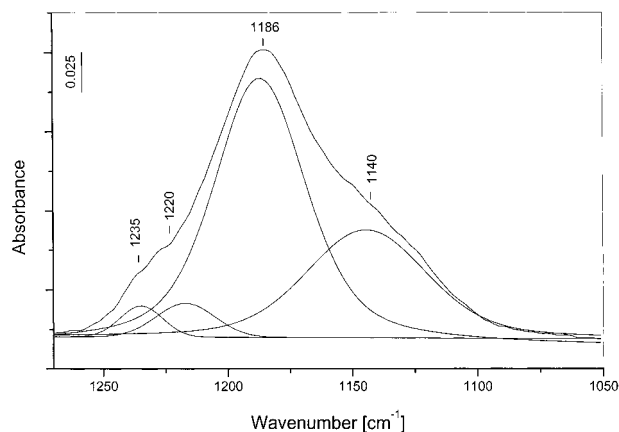
### Adsorption of NO on Zirconia at Room Temperature.

Most of the bands observed during the contact of NO (1.07 kPa) with the surface of the zirconia samples with different degrees of hydroxylation or after partial deuterioxylation, develop with time (the spectra are not shown). For all of the samples studied, a negative band at 3650–3630  $\text{cm}^{-1}$  (2696  $\text{cm}^{-1}$  in the case of the ZHD sample) is observed indicating alteration of bridged OH groups. The intensity of this band reaches a maximum approximately 20 min after the introduction of NO to the IR cell and then starts gradually to decrease. At the same time, a broad band in the 3500–3000/2700–2300  $\text{cm}^{-1}$  region due to H/D-bonded OH/OD groups develops and increases steadily in intensity.

The spectra of adsorbed NO (1.07 kPa) at room temperature for a period of 60 min on samples Z, ZH, and ZHD are shown in Figure 2. The intensities of the bands at 2285, 2244, and 1912  $\text{cm}^{-1}$  do not change with time and appear less intense in the case of wet samples (compare spectra a–c in Figure 2). After evacuation for 15 min at room temperature, the bands at 2285 and 2244  $\text{cm}^{-1}$  decrease strongly in intensity, whereas the band at 1912  $\text{cm}^{-1}$  disappears from the spectrum. This behavior is illustrated in the spectrum of sample Z (Figure 2,



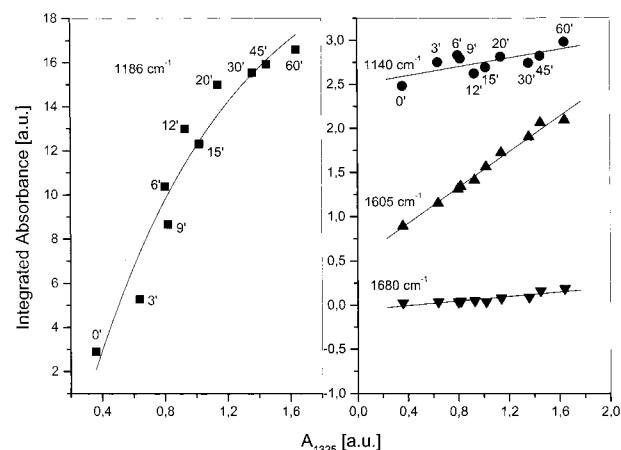
**Figure 2.** FTIR spectra of NO (1.07 kPa) adsorbed at room temperature for a period of 60 min on samples (a) Z, (b) ZH, and (c) ZHD and (d) after evacuation of sample Z at room temperature for 15 min.



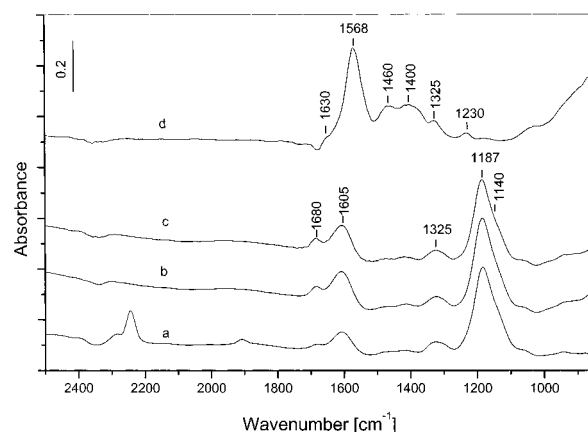
**Figure 3.** Results of the curve-fitting procedure applied to the FTIR spectrum in the 1270–1050 cm<sup>–1</sup> region taken after 15 min of NO adsorption (1.07 kPa, room temperature) on the ZH sample.

spectrum d), which shows that the evacuation also leads to the disappearance of the shoulder at 1230 cm<sup>–1</sup> of the band at 1186 cm<sup>–1</sup>. Judging from this behavior, the bands at 2285, 2244, and approximately 1230 cm<sup>–1</sup> are attributed to N<sub>2</sub>O<sup>12,14,15,24</sup> probably adsorbed on two different surface sites. The absorption at 1912 cm<sup>–1</sup> is assigned to Zr<sup>4+</sup>–NO species.<sup>13–15</sup> All other bands grow with time in the presence of gaseous NO, and their intensities increase with increasing degree of sample hydroxylation (compare spectra a and b in Figure 2). Partial deuteroxylation (sample ZHD) leads to a lowering of the intensity of the band at 1605 cm<sup>–1</sup> compared to that in the Z and ZH samples and the appearance of an additional absorption at 1403 cm<sup>–1</sup> (Figure 2, spectrum c). From this result, the bands at 1605 and 1403 cm<sup>–1</sup> are assigned to  $\delta$ (H<sub>2</sub>O) and  $\delta$ (HOD), respectively, of adsorbed water.<sup>25</sup> The corresponding  $\nu$ (OH/OD) stretching modes are observed in the 3500–3000/2700–2300 cm<sup>–1</sup> region.

The band at 1186 cm<sup>–1</sup> (Figure 2, spectra a–c) has a higher intensity in the case of wet samples (ZH and ZHD). This band has a complex shape. The results of curve fitting of the spectrum taken after 15 min of NO adsorption on the ZH sample in the 1270–1050 cm<sup>–1</sup> region are shown in Figure 3. The weak bands at 1235 and 1220 cm<sup>–1</sup> are due to  $\nu$ (NO) stretching modes of adsorbed N<sub>2</sub>O (two types).<sup>12,14,15,24</sup> Curve fitting was applied to all of the spectra taken within a period of 60 min of NO adsorption, and the dependence of the integrated absorbance of the band at 1186 cm<sup>–1</sup> on the integrated absorbances of the bands at 1680, 1605, 1325, and 1140 cm<sup>–1</sup> was examined. In all of these cases, no linear correlation was found, which



**Figure 4.** Correlation between the integrated absorbances of the species in the 1200–1100 cm<sup>–1</sup> region produced during NO adsorption (1.07 kPa, room temperature) at various times on sample ZH.



**Figure 5.** FTIR spectra of NO (1.07 kPa) (a) adsorbed on sample ZH at room temperature for 60 min, (b) followed by evacuation for 15 min at room temperature, (c) after subsequent addition of 1.33 kPa of oxygen, and (d) after heating of the closed IR cell for 10 min at 573 K.

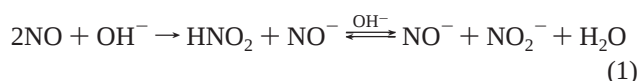
indicates that this band corresponds to one NO<sub>x</sub> species. Figure 4 displays the plots of the integrated absorbances of the bands at 1680, 1605, 1186, and 1140 cm<sup>–1</sup> versus the integrated absorbance of the band at 1325 cm<sup>–1</sup> at various times of NO adsorption. The linear relationship between the intensities of the bands at 1680, 1605, 1140, and 1325 cm<sup>–1</sup> suggests either that they belong to one surface species, or that the species characterized by the corresponding bands are produced in a common process. The bands at 1680 and 1140 cm<sup>–1</sup> most probably characterize one surface species because their intensities change almost in parallel. On the basis of the literature data,<sup>12,24,26</sup> they are assigned to the  $\nu$ (N=O) and  $\delta$ (NOH) modes, respectively, of *cis*-HNO<sub>2</sub> formed on the surface of zirconia.

Taking into account that the band at 1605 cm<sup>–1</sup> is due to adsorbed water molecules, it is concluded that water and the species at 1325 cm<sup>–1</sup> are produced simultaneously by one and the same reaction. The latter band is attributed to superimposition of the  $\nu_{as}$ (NO<sub>2</sub>) and  $\nu_s$ (NO<sub>2</sub>) modes of NO<sub>2</sub><sup>–</sup> nitro species.<sup>9,25,27</sup>

Figure 5 shows the spectrum of adsorbed NO (1.07 kPa) on the ZH sample for 60 min (spectrum a) followed by evacuation for 15 min at room temperature (spectrum b). Oxygen (1.33 kPa) was added to the sample treated in this way (spectrum c). This procedure does not affect the intensity of the bands in the 2500–1000 cm<sup>–1</sup> region. However, the band at 1186 cm<sup>–1</sup>

disappears after heating the closed IR cell (without evacuation) for 10 min at 573 K, and a series of new bands in the 1650–1200  $\text{cm}^{-1}$  region is observed instead (Figure 5, spectrum d). The strong band at 1568  $\text{cm}^{-1}$  is typical of surface bidentate nitrate species.<sup>9,27</sup> This species can be produced by the disproportionation of nitrous acid, which is known to be unstable on heating. Indeed, the band at 1680  $\text{cm}^{-1}$  due to the  $\nu(\text{N}=\text{O})$  mode of  $\text{HNO}_2$  disappears from the spectrum. The products of  $\text{HNO}_2$  disproportionation,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{NO}$ , give rise to nitrate species (1568  $\text{cm}^{-1}$ ) and adsorbed water molecules (shoulder at approximately 1630  $\text{cm}^{-1}$ ). In the oxygen atmosphere, the  $\text{NO}$  evolved can be oxidized to  $\text{NO}_2$  and then adsorbed as nitrate species. The bands at 1460 and 1400  $\text{cm}^{-1}$  correspond to  $\nu(\text{N}=\text{O})$  modes of monodentate nitrito species.<sup>27</sup> Probably, the nitro species (band at 1325  $\text{cm}^{-1}$ ), which are obtained during the  $\text{NO}$  adsorption, are not affected by the treatment with oxygen. It is known that nitro compounds are stable in oxygen atmosphere.<sup>28</sup> Finally, the species that are characterized by the band at 1186  $\text{cm}^{-1}$  and disappear after oxidation contribute to the formation of surface nitrate and nitrite compounds. This indicates that this adsorption form contains nitrogen in a low oxidation state and undergoes oxidation under the conditions described.

The formation of the surface species observed during the adsorption of  $\text{NO}$  on the surface of zirconia and the changes in their surface concentrations with time can be explained assuming the following reaction

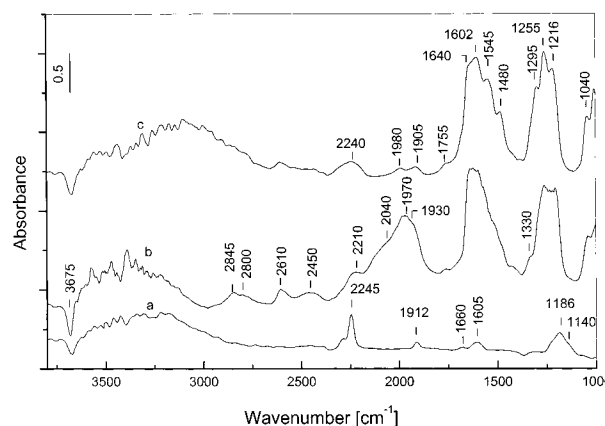


According to this process,  $\text{NO}$  undergoes disproportionation with participation of the bridged  $\text{OH}$  groups of zirconia to *cis*- $\text{HNO}_2$  and anionic nitrosyl,  $\text{NO}^-$ . The band at 1186  $\text{cm}^{-1}$  is assigned to the latter species. The nitrous acid produced partially dissociates to nitro species (1325  $\text{cm}^{-1}$ ), evolving protons, which recombine with surface hydroxyls to form water molecules or recombine with coordinatively unsaturated oxide ions. The latter process leads to partial restoration of the consumed hydroxyls. This can explain the observed gradual decrease in the intensity of the negative band at 3650  $\text{cm}^{-1}$  in the later stages of  $\text{NO}$  adsorption. The experimental data show that the occurrence of reaction 1 is favored by wet surfaces.

The proposed interpretation of the band at 1186  $\text{cm}^{-1}$  disagrees with its assignments to surface nitrites<sup>10,13,15</sup> and monodentate nitrates<sup>12</sup> offered in the literature. Anionic nitrosyl species have been observed when  $\text{NO}$  is adsorbed on alkaline earth metal oxides such as  $\text{MgO}$ <sup>29</sup> and  $\text{CaO}$ ,<sup>30</sup> on lanthanide metal oxides such as  $\text{CeO}_2$ <sup>31</sup> and  $\text{La}_2\text{O}_3$ ,<sup>27,32</sup> and on  $\text{TiO}_2$ .<sup>28</sup>

The evacuation for 15 min at room temperature of all of the samples studied causes a slight increase in the intensities of the bands at 1680, 1605, 1325, and 1186  $\text{cm}^{-1}$  due to adsorbed  $\text{HNO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2^-$ , and  $\text{NO}^-$  species, respectively (see Figure 2, spectra a and d, and Figure 5, spectra a and b). Enhancement in the intensity of the H-bonded  $\text{OH}$  groups is also observed, which is accompanied by a decrease in the intensity of the negative band due to alteration of the bridged hydroxyls at 3650  $\text{cm}^{-1}$  (Figure 2, spectra a and d). These changes most probably are caused by transformation of the nitrosyls coordinated to the  $\text{Zr}^{4+}$  ions according to reaction 1.

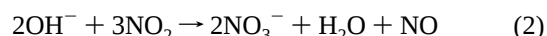
Finally it should be pointed out that adsorbed  $\text{N}_2\text{O}$  is observed often upon adsorption of  $\text{NO}$  on zeolites and oxides.<sup>9</sup> In the case of zirconia, it can be produced by the adsorption of  $\text{NO}$  on an oxygen pair of vacancy sites as proposed for  $\text{La}_2\text{O}_3$  by Huang et al.<sup>27</sup>



**Figure 6.** FTIR spectra of  $\text{NO}$  (2.0 kPa) (a) adsorbed on sample Z at room temperature for 30 min, (b) after subsequent introduction of 4.27 kPa of oxygen, and (c) after evacuation for 15 min at room temperature.

**Coadsorption of  $\text{NO}$  and  $\text{O}_2$  on Zirconia at Room Temperature.** Spectrum b in Figure 6 was obtained after the subsequent introduction of 4.27 kPa of oxygen into the IR cell containing 2.0 kPa of  $\text{NO}$  (spectrum a in the same figure taken 30 min after  $\text{NO}$  adsorption). It should be noted, that immediately after the admission of oxygen, the color of the gas phase changed to brown, indicating that a considerable amount of  $\text{NO}_2$  was formed. This causes drastic changes in the spectrum of preadsorbed  $\text{NO}$  (Figure 6, spectrum b). The bands at 1186 and 1140  $\text{cm}^{-1}$  disappear, and two unresolved and intense bands in the 1700–1150  $\text{cm}^{-1}$  region appear. A poorly resolved absorption at 1040  $\text{cm}^{-1}$  is also detected. In the 2250–1700  $\text{cm}^{-1}$  region a broad, complex absorption is observed. In addition, weak bands at 2845, 2800, 2610, 2450, and 1755  $\text{cm}^{-1}$  are detected. In the  $\text{OH}$  region, the negative band at 3675  $\text{cm}^{-1}$  due to the altered, bridged  $\text{OH}$  groups increases in intensity and is accompanied by an enhancement in the positive absorption at 3600–3000  $\text{cm}^{-1}$ .

The strong absorption in the 1700–1150  $\text{cm}^{-1}$  region is due to the formation of surface nitrates and is attributed to the  $\nu_3$  spectral splitting of adsorbed  $\text{NO}_3^-$  ions differing in their types of coordination.<sup>9,13,27</sup> The band at 1040  $\text{cm}^{-1}$  is assigned to the  $\nu_s(\text{NO}_2)$  mode.<sup>9,13,27</sup> The nitrate species can form by disproportionation of  $\text{NO}_2$  with the participation of the surface  $\text{OH}$  groups



The appearance of a negative band at 3675  $\text{cm}^{-1}$  and the broad positive absorption in the 3600–3000  $\text{cm}^{-1}$  region supports the occurrence of this process. Similar interaction was observed to occur during the adsorption of  $\text{NO}_2$  on titania (anatase).<sup>33,34</sup> Another possibility for the formation of nitrate species involves disproportionation of  $\text{NO}_2$  on surface Lewis acid–base pairs according to the reaction<sup>28,33</sup>



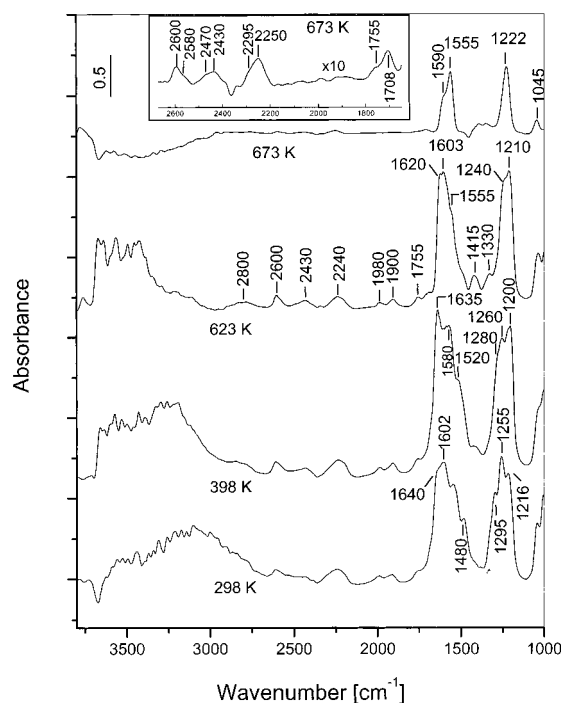
The N–O stretching frequency of nitrosonium ion adsorbed on surfaces is found at 2290–2102  $\text{cm}^{-1}$ .<sup>9,28,33–35</sup> Spectrum b in Figure 6 displays a broad, poorly resolved absorption at approximately 2210  $\text{cm}^{-1}$ , which loses intensity after evacuation at room temperature for 15 min and shifts to 2240  $\text{cm}^{-1}$ . However, the behavior of the band at 2240  $\text{cm}^{-1}$  under evacuation at higher temperatures (see below) demonstrates that it is not associated with adsorbed  $\text{NO}^+$  ions.

The complex band in the 2200–1700  $\text{cm}^{-1}$  region with a maximum at 1970  $\text{cm}^{-1}$  (Figure 6, spectrum b) falls in the

spectral region typical for the coordination of NO on strong Lewis acid sites. The assignment of the feature at 1970 cm<sup>-1</sup> is made by taking into account the behavior of the weak bands at 1980 and 1905 cm<sup>-1</sup> that are observed after evacuation at room temperature. These bands resist high-temperature vacuum treatment (see below) and are not associated with nitrosylic species. The band at 1970 cm<sup>-1</sup> appears in the spectrum when large amounts of surface nitrates are present. For this reason, in accordance with the literature data,<sup>12</sup> we assign this band to Zr<sup>4+</sup>-NO nitrosyls that have NO<sub>3</sub><sup>-</sup> species in their coordination sphere, i.e., to the complex (ON)-Zr<sup>4+</sup>-(NO<sub>3</sub><sup>-</sup>). The absorption at 1930 cm<sup>-1</sup> can be attributed to a second (ON)-Zr<sup>4+</sup>-(NO<sub>3</sub><sup>-</sup>) species or to adsorbed N<sub>2</sub>O<sub>3</sub>. Because evacuation causes simultaneous disappearance of the band positioned at approximately 1330 cm<sup>-1</sup>, we prefer to assign the features at 1930 and 1330 cm<sup>-1</sup> to  $\nu(\text{N}=\text{O})$  and  $\nu_s(\text{NO}_2)$  modes, respectively, of adsorbed N<sub>2</sub>O<sub>3</sub>. This species forms during NO and O<sub>2</sub> coadsorption on various oxide systems and is removed easily by evacuation at room temperature.<sup>9</sup> The N<sub>2</sub>O<sub>3</sub> molecule adsorbed on zeolites produces a  $\nu(\text{N}=\text{O})$  stretching vibration in the 1930–1880 cm<sup>-1</sup> region, the  $\nu_{as}(\text{NO}_2)$  modes appear at 1590–1550 cm<sup>-1</sup>, and the modes due to  $\nu_s(\text{NO}_2)$  are detected at 1305–1290 cm<sup>-1</sup>.<sup>9</sup> The shoulder at 2040 cm<sup>-1</sup>, which disappears after evacuation at room temperature, is tentatively assigned to NO<sub>2</sub><sup>δ+</sup>.

After removal of the gaseous phase by evacuation at room temperature, the bands in the nitrate region are better resolved (Figure 6, spectrum c). The changes in the two major band envelopes in the 1700–1000 cm<sup>-1</sup> region suggest that, most probably, some desorption/decomposition of the species has occurred. It can be seen that the bands at 2610 and 2450 cm<sup>-1</sup> appear in the spectrum with reduced intensity. The bands at 2845 and 2800 cm<sup>-1</sup> are covered by the absorption due to H-bonded OH groups, and their behavior under these conditions cannot be followed. In addition, two weak bands at 1980 and 1905 cm<sup>-1</sup> are detected.

An attempt to assign the bands in the nitrate region was made by following the changes in the spectra obtained under vacuum treatment at elevated temperatures. Study of the thermal stability of the adsorption forms produced during interaction of zirconia with the NO/O<sub>2</sub> mixture (Figure 7) shows that the majority of species formed at room temperature are still present after heating in a vacuum for 10 min at 623 K. (The spectra were recorded after the IR cell had been cooled to room temperature). The changes in the shapes and intensities of the nitrate bands indicate that in the temperature range 298–398 K, rearrangement rather than decomposition of the NO<sub>3</sub><sup>-</sup> species has occurred. For example, the band at about 1480 cm<sup>-1</sup> is not visible after heating at 398 K, but the intensities of the nitrate bands at 1635, 1580, and 1520 cm<sup>-1</sup>, together with that of the complex band at 1280–1200 cm<sup>-1</sup>, have increased. An increase in the intensities of the weak bands in the 3000–1700 cm<sup>-1</sup> region is also detected. Noticeable decomposition of the nitrate species begins at 623 K. After evacuation at 673 K, the absorption in the 3000–1700 cm<sup>-1</sup> region becomes very weak, and the bands in the nitrate region appear with strongly reduced intensity. The negative band in the OH region shows that the hydroxyl groups are not completely restored and that some of them are lost during high-temperature evacuation. From the results of the thermal stability and the magnitude of the  $\nu_3$  spectral splitting,<sup>9,13,27</sup> the nitrate bands can be assigned to bridged (1640–1620 and 1216–1200 cm<sup>-1</sup>), bidentate (1602–1590 and 1260–1240 cm<sup>-1</sup>, 1580–1545 and 1222–1210 cm<sup>-1</sup>, 1520 and 1280 cm<sup>-1</sup>), and monodentate (1480 and 1295 cm<sup>-1</sup>) species. The weak bands



**Figure 7.** FTIR spectra obtained after heating of sample Z containing preadsorbed NO<sub>x</sub> species for 15 min in a vacuum at various temperatures. This spectrum (298 K) corresponds to spectrum c in Figure 6.

at 1415 and 1330 cm<sup>-1</sup>, which are more visible after treatment at 623 K, are attributed to monodentate nitro compounds.<sup>27</sup>

The weak bands at 2845, 2800, 2610, 2450, 2240, 1980, 1905, and 1755 cm<sup>-1</sup> (Figures 6 and 7) are due to combination modes of the nitrates species.<sup>24</sup> These features are detected during NO/O<sub>2</sub> coadsorption, which results in the formation of a large amount of surface nitrate species. This assignment is supported by the experiments showing the thermal stability of nitrate species. The bands in the 3000–1700 cm<sup>-1</sup> region follow the behavior of the fundamental nitrate bands. Combination bands at 2610, 2580, and 2520 cm<sup>-1</sup> due to different kinds of nitrates on the surface of zirconia and the overtone band at 2444 cm<sup>-1</sup> of nitrito species were also reported by Hadjiivanov.<sup>12</sup>

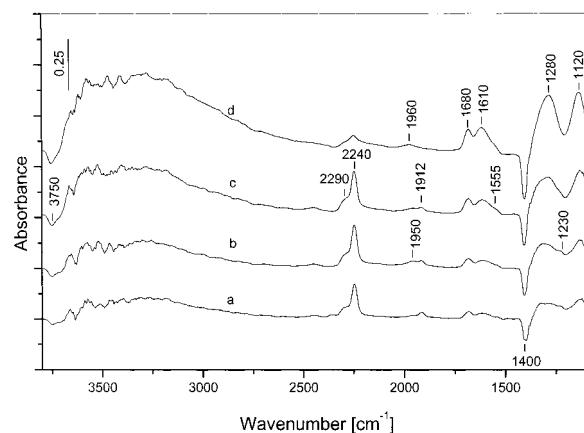
It is difficult to propose an unambiguous assignment for the combination bands of the species in the nitrate region because the fundamental bands below 1000 cm<sup>-1</sup> cannot be detected. We start with the spectrum obtained after evacuation for 10 min at 673 K, which is characterized by the lowest concentration of surface nitrates. The spectrum exhibits bands corresponding to the  $\nu_3$  spectral splitting of two types of bidentate nitrates: 1590 [ $\nu(\text{N}=\text{O})$ ] and 1222 cm<sup>-1</sup> [ $\nu_{as}(\text{NO}_2)$ ] and 1555 [ $\nu(\text{N}=\text{O})$ ] and 1222 cm<sup>-1</sup> [ $\nu_{as}(\text{NO}_2)$ ]. The  $\nu_s(\text{NO}_2)$  stretching vibration is at 1045 cm<sup>-1</sup>. From the inset in Figure 7, it can be seen that the band at 2600 cm<sup>-1</sup> with a shoulder at 2580 cm<sup>-1</sup> corresponds to a binary combination between the  $\nu(\text{N}=\text{O})$  vibrations at 1590 and 1555 cm<sup>-1</sup> and the  $\nu_s(\text{NO}_2)$  mode at 1045 cm<sup>-1</sup>. The combinations between the  $\nu_{as}(\text{NO}_2)$  mode at 1222 cm<sup>-1</sup> and the  $\nu_s(\text{NO}_2)$  mode at 1045 cm<sup>-1</sup> give rise to the absorption with a maximum at 2250 cm<sup>-1</sup>. This band has a high-frequency shoulder positioned at about 2295 cm<sup>-1</sup>. This implies that the fundamental band at 1222 cm<sup>-1</sup> should contain a weaker component at approximately 1260 cm<sup>-1</sup>, which is the contaminant band of that at 1590 cm<sup>-1</sup>. The existence of an unresolved absorption in the region of the band at 1222 cm<sup>-1</sup> can explain the relatively high intensity of the latter relative to that of the bands at 1590 and 1555 cm<sup>-1</sup>. The band at 2430 cm<sup>-1</sup> is the first overtone of the band at 1222 cm<sup>-1</sup>. Again, this band has a

**TABLE 1: Assignments of the FTIR Bands Observed during Adsorption of 1.07 kPa of NO and Its Coadsorption with O<sub>2</sub> (NO:O<sub>2</sub> = 1:2) at Room Temperature on Zirconia**

| NO <sub>x</sub> species                              | band positions (cm <sup>-1</sup> ) | modes                                                 |
|------------------------------------------------------|------------------------------------|-------------------------------------------------------|
| N <sub>2</sub> O (ads)                               | 2285, 2244                         | $\nu(\text{NN})$                                      |
|                                                      | 1230                               | $\nu(\text{NO})$                                      |
| Zr <sup>4+</sup> -NO                                 | 1912                               | $\nu(\text{NO})$                                      |
| ON-Zr <sup>4+</sup> -(NO <sub>3</sub> <sup>-</sup> ) | 1970                               | $\nu(\text{NO})$                                      |
| N <sub>2</sub> O <sub>3</sub>                        | 1930                               | $\nu(\text{N=O})$                                     |
|                                                      | 1330                               | $\nu_s(\text{NO}_2)$                                  |
| <i>cis</i> -HNO <sub>2</sub> (ads)                   | 1680                               | $\nu(\text{N=O})$                                     |
|                                                      | 1140                               | $\delta(\text{NOH})$                                  |
| H <sub>2</sub> O (ads)                               | 3550–3000                          | $\nu(\text{OH})$                                      |
|                                                      | 1605                               | $\delta(\text{HOH})$                                  |
| NO <sub>2</sub> <sup>-</sup> (nitro)                 | 1325                               | $\nu_{\text{as}}(\text{NO}_2)$ , $\nu_s(\text{NO}_2)$ |
| NO <sup>-</sup>                                      | 1186                               | $\nu(\text{NO})$                                      |
| NO <sub>3</sub> <sup>-</sup> (bridged)               | 1640–1620                          | $\nu(\text{N=O})$                                     |
|                                                      | 1216–1200                          | $\nu_{\text{as}}(\text{NO}_2)$                        |
|                                                      | 1040                               | $\nu_s(\text{NO}_2)$                                  |
|                                                      | 2845, 2800                         | $\nu(\text{N=O}) + \nu_{\text{as}}(\text{NO}_2)$      |
|                                                      | ~2240                              | $\nu_{\text{as}}(\text{NO}_2) + \nu_s(\text{NO}_2)$   |
|                                                      | 1980, 1900–1905                    | $\nu_s(\text{NO}_2) + \delta(\text{ONO})$             |
| NO <sub>3</sub> <sup>-</sup> (bidentate)             | 1602–1590, 1580–1545, 1520         | $\nu(\text{N=O})$                                     |
|                                                      | 1260–1240, 1222–1210, 1280         | $\nu_{\text{as}}(\text{NO}_2)$                        |
|                                                      | 1040                               | $\nu_s(\text{NO}_2)$                                  |
|                                                      | 2600, 2580                         | $\nu(\text{N=O}) + \nu_s(\text{NO}_2)$                |
|                                                      | 2470, 2430                         | $2\nu_{\text{as}}(\text{NO}_2)$                       |
|                                                      | 2295, 2250                         | $\nu_{\text{as}}(\text{NO}_2) + \nu_s(\text{NO}_2)$   |
|                                                      | 1755, (1708)                       | $\nu_s(\text{NO}_2) + \delta(\text{ONO})$             |
| NO <sub>3</sub> <sup>-</sup> (monodentate)           | 1480                               | $\nu_{\text{as}}(\text{NO}_2)$                        |
|                                                      | 1295                               | $\nu_s(\text{NO}_2)$                                  |

high-frequency shoulder at about 2470 cm<sup>-1</sup>, which confirms the assumption that there is an unresolved absorption at approximately 1260 cm<sup>-1</sup>. This interpretation disagrees with the conclusion made by Hadjiivanov<sup>12</sup> that an analogous band observed at 2440 cm<sup>-1</sup> is due to the first overtone of a band at 1220 cm<sup>-1</sup> associated with nitrito species, which are formed during thermal decomposition of surface nitrates on zirconia.

The weak bands at 1980, 1900, and 1755 cm<sup>-1</sup> (see Figures 6 and 7) probably are due to combinations between the  $\nu_s(\text{NO}_2)$  (1045 cm<sup>-1</sup>) and  $\delta(\text{ONO})$  (in-plane bending) modes. This assignment is based on the fact that the combination band [ $\nu_s(\text{NO}_2) + \delta(\text{ONO})$ ] of free NO<sub>3</sub><sup>-</sup> ion appears in the 1800–1700 cm<sup>-1</sup> region.<sup>24,25,36</sup> Upon coordination in bulk compounds, the  $\delta(\text{ONO})$  mode splits into two bands giving rise to two [ $\nu_s(\text{NO}_2) + \delta(\text{ONO})$ ] combination bands.<sup>36</sup> The maximum separation between the latter is 66 cm<sup>-1</sup> for bidentate nitrate ion and 26 cm<sup>-1</sup> for monodentate species.<sup>36</sup> Thus, it can be proposed that the pair of bands at 1980 and 1900 cm<sup>-1</sup> is associated with [ $\nu_s(\text{NO}_2) + \delta(\text{ONO})$ ] modes of bridged NO<sub>3</sub><sup>-</sup> species (spectral splitting of 80 cm<sup>-1</sup>), whereas the band at 1755 cm<sup>-1</sup> and probably that at 1708 cm<sup>-1</sup> (see the inset in Figure 7) are indicative of the presence of bidentate NO<sub>3</sub><sup>-</sup> ion (spectral splitting of approximately 50 cm<sup>-1</sup>). The latter absorption is masked by the band at 1630–1600 cm<sup>-1</sup> and can be detected after heating the sample in a vacuum at 673 K. Under these conditions, the broad absorption with a maximum at 2800 cm<sup>-1</sup> and the pair of bands at 1980 and 1900 cm<sup>-1</sup> have disappeared, and the spectrum in the fundamental nitrate region contains bands associated with bidentate nitrates. It can be concluded that the bands at 2845 and 2800 cm<sup>-1</sup> (Figures 6 and 7) are due to a combination between the  $\nu(\text{N=O})$  (ca. 1640–1620 cm<sup>-1</sup>) and  $\nu_{\text{as}}(\text{NO}_2)$  (ca. 1210 cm<sup>-1</sup>) modes of the bridged nitrates. Finally, a combination between the  $\nu_{\text{as}}(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  vibrations of the bridged nitrates should contribute to the absorption at 2240 cm<sup>-1</sup> when these NO<sub>3</sub><sup>-</sup> species are present on the surface of zirconia, i.e., in the 298–623 K temperature range of evacuation (Figure 7). These considerations show that the combination region of the spectra can be used

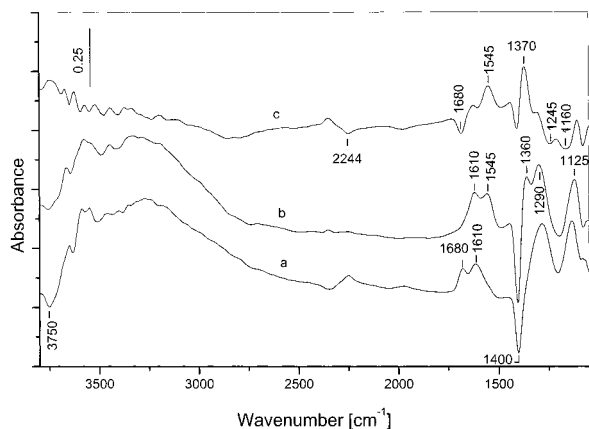
**Figure 8.** FTIR spectra of NO (1.07 kPa) adsorbed on sample ZS at room temperature for various times. The spectra are taken (a) immediately after NO admission, (b) after 12 min, (c) after 60 min, and (d) after evacuation for 15 min at room temperature.

for structural identification of bidentate and bridged nitrates. The proposed application of the combination region<sup>12</sup> for distinguishing between nitrate and nitrito surface compounds on the basis of the presence (or absence) of an overtone band at 2440 cm<sup>-1</sup> requires further evidence.

The absorption bands observed on zirconia after exposure to either NO or a NO/O<sub>2</sub> mixture are summarized in Table 1.

**Adsorption of NO at Room Temperature on Sulfated Zirconia.** The evolution of the spectra of adsorbed NO (1.07 kPa, room temperature) on the ZS sample with time is shown in Figure 8. As in the case of the unpromoted sample, the bands at 2290, 2240, and about 1230 cm<sup>-1</sup> are due to adsorbed N<sub>2</sub>O, whereas the weak broad band at 1950 cm<sup>-1</sup> is assigned to NO adsorbed on Zr<sup>4+</sup> ions that have sulfate groups in the vicinity.<sup>11</sup> This absorption appears at higher frequency because of the increased acidity of the adsorption site caused by the electron-withdrawing SO<sub>4</sub><sup>2-</sup> species. The absorption at 1912 cm<sup>-1</sup> corresponds to the N–O stretching vibration of NO coordinated to Zr<sup>4+</sup> sites that are not perturbed by sulfate groups. The bands due to adsorbed N<sub>2</sub>O and Zr<sup>4+</sup>-NO nitrosyls reach saturation within a period of 6 min. All other bands continue to grow up to 45 min of NO adsorption.

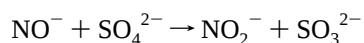
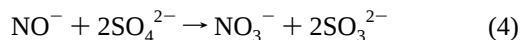
A noticeable difference between the pure and sulfated zirconia is that, in the latter case, the altered OH groups are at 3750 cm<sup>-1</sup>, i.e., terminal hydroxyls are involved in interactions with NO, leading to the development of a positive absorption between 3600 and 3000 cm<sup>-1</sup>. The difference in reactivity of the hydroxyl groups on zirconia in the presence or absence of SO<sub>4</sub><sup>2-</sup> ions can be explained by assuming that sulfate ions replace some of the topmost bridged hydroxyl groups and that the remaining ones are not involved in disproportionation of NO. As in the case of pure zirconia, the bands at 1680 and 1610 cm<sup>-1</sup>, due to adsorbed HNO<sub>2</sub> and H<sub>2</sub>O, grow with time. A weakly resolved component at approximately 1555 cm<sup>-1</sup> develops as well. The increase in intensity of the negative band at 1400 cm<sup>-1</sup>, due to terminal S=O bonds, indicates that a perturbation of the sulfate groups occurs. A broad, poorly resolved absorption in the 1390–1200 cm<sup>-1</sup> region and a band at 1120 cm<sup>-1</sup> grow with the extent of NO exposure. A similar set of bands has been observed upon adsorption of water on sulfated zirconia<sup>21</sup> and is assigned to split  $\nu_3$  mode of bidentate sulfato complex of C<sub>2v</sub> symmetry. Obviously, the water molecules produced upon NO adsorption affect the structure of the original sulfate groups. In contrast to the adsorption of NO on pure zirconia, no band at 1186 cm<sup>-1</sup> is detected.



**Figure 9.** FTIR spectra of NO (1.07 kPa) adsorbed on sample ZS for 60 min followed by evacuation for 15 min at room temperature and (a) after subsequent addition of 1.33 kPa of oxygen and (b) after heating of the closed IR cell for 10 min at 573 K. Spectrum c was obtained by the subtraction of spectrum b from spectrum a.

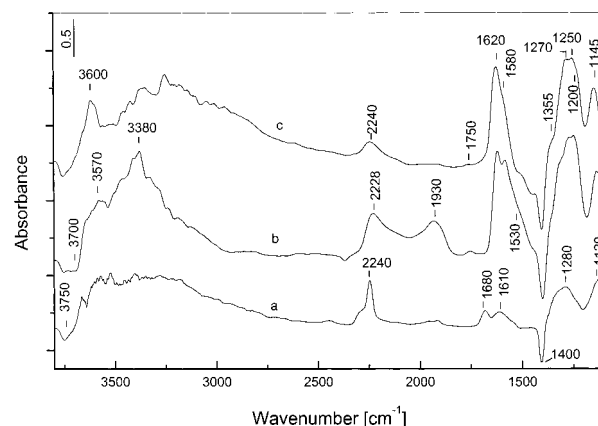
Evacuation for 15 min at room temperature (Figure 8, spectrum d) leads to an increase in the intensity of both positive and negative bands in the 1700–1000 cm<sup>–1</sup> region, which is accompanied by an enhancement of the intensities of the negative band at 3750 cm<sup>–1</sup> and the positive absorption in the region of the H-bonded OH groups. The bands due to adsorbed N<sub>2</sub>O (2290 and 2240 cm<sup>–1</sup>) appear with reduced intensity, and the absorption at 1912 cm<sup>–1</sup> due to Zr<sup>4+</sup>–NO species disappears. The band at 1950 cm<sup>–1</sup> shifts to 1960 cm<sup>–1</sup> and resists evacuation, which confirms that it is associated with NO adsorbed on strong Lewis acid sites.

It is difficult to propose a straightforward interpretation of the experimental results obtained during the adsorption of NO on sulfated zirconia, because of the existence of overlapping bands in the 1500–1000 cm<sup>–1</sup> region arising from simultaneous alteration of the sulfate groups and formation of NO<sub>x</sub> adsorbed species. The fact that adsorbed water and nitrous acid are detected implies that a process analogous to that described by reaction 1 occurs in the case of the ZS sample. However, no absorption that can be assigned to an anionic nitrosyl, NO<sup>–</sup>, is observed. It can be proposed that NO<sup>–</sup> species also form in this case but are oxidized fast by sulfate ions, for example, to NO<sub>3</sub><sup>–</sup> and NO<sub>2</sub><sup>–</sup> species according to the reactions



The vibrational modes of the free SO<sub>3</sub><sup>2–</sup> ion are below 1000 cm<sup>–1</sup>.<sup>25</sup> In bulk compounds,<sup>25</sup> if coordination occurs through the sulfur atom, the ν<sub>as</sub>(S–O) mode shifts to 1100–1050 cm<sup>–1</sup>. In the case of O bonding, this mode splits into two and falls in the 900–850 cm<sup>–1</sup> region. Because of their poor quality, the spectra below 1050 cm<sup>–1</sup> are not informative, and the formation of coordinated SO<sub>3</sub><sup>2–</sup> species cannot be proven. However, the shoulder at approximately 1555 cm<sup>–1</sup> (Figure 8) can be assigned to nitrate species. In the case of NO adsorption on pure zirconia, this band is not observed (Figure 2), which can support the occurrence of reaction 4. The NO<sub>2</sub><sup>–</sup> species (nitro and nitrito) exhibit characteristic bands in the 1400–1000 cm<sup>–1</sup>,<sup>27</sup> but if formed, these bands cannot be observed because of overlap with the absorption due to perturbed sulfate groups.

The addition of 1.33 kPa of oxygen (spectrum a in Figure 9) at room temperature to the sample evacuated after NO adsorp-



**Figure 10.** FTIR spectra of NO (2.0 kPa) (a) adsorbed on sample ZS at room temperature for 30 min, (b) after subsequent introduction of 4.27 kPa of oxygen, and (c) after evacuation for 15 min at room temperature.

tion (spectrum d in Figure 8) does not cause any changes. Heating of the closed IR cell for 10 min at 573 K leads to the disappearance of the bands at 2244 and 1680 cm<sup>–1</sup> due to adsorbed N<sub>2</sub>O and HNO<sub>2</sub>, respectively (Figure 9, spectrum b). New bands at 1545 and 1360 cm<sup>–1</sup> are detected. Spectrum c in Figure 9 (obtained by the subtraction of spectrum b from spectrum a) illustrates the changes described. In addition, it shows the existence of two negative bands at 1245 and 1160 cm<sup>–1</sup>. The band at 1545 cm<sup>–1</sup> can be assigned to nitrate NO<sub>3</sub><sup>–</sup> species. The negative bands at 1245 and 1160 cm<sup>–1</sup> are due to ν(N–O) and δ(NOH) modes of decomposed N<sub>2</sub>O and HNO<sub>2</sub>, respectively. It is known that N<sub>2</sub>O is also an unstable compound and decomposes rapidly to N<sub>2</sub> and O<sub>2</sub> when heated. Probably, the nitrate species produced are localized in the vicinity of the sulfate groups. This causes a perturbation of the latter, as evidenced by an additional increase in the intensity of the negative band at 1400 cm<sup>–1</sup> and the appearance of a positive band at 1360 cm<sup>–1</sup>. The suggestion that the nitrate species affect the sulfate groups is supported further by the experiments of NO/O<sub>2</sub> coadsorption where large amounts of NO<sub>3</sub><sup>–</sup> ions are formed (see below). However, the increase in intensity of the positive band at 1370 cm<sup>–1</sup> is greater than the corresponding decrease in intensity of the band at 1400 cm<sup>–1</sup> due to alteration of sulfate groups (Figure 10, spectrum c). It can be assumed that treatment with oxygen causes oxidation of SO<sub>3</sub><sup>2–</sup> species (see reaction 4). The restored sulfate groups can have localization on the zirconia surface that differs from that of the original SO<sub>4</sub><sup>2–</sup> species. This difference contributes to the absorption at 1360 cm<sup>–1</sup>. It is also possible that there is a band contaminant to that at 1545 cm<sup>–1</sup>, which is superimposed to that at 1360 cm<sup>–1</sup>.

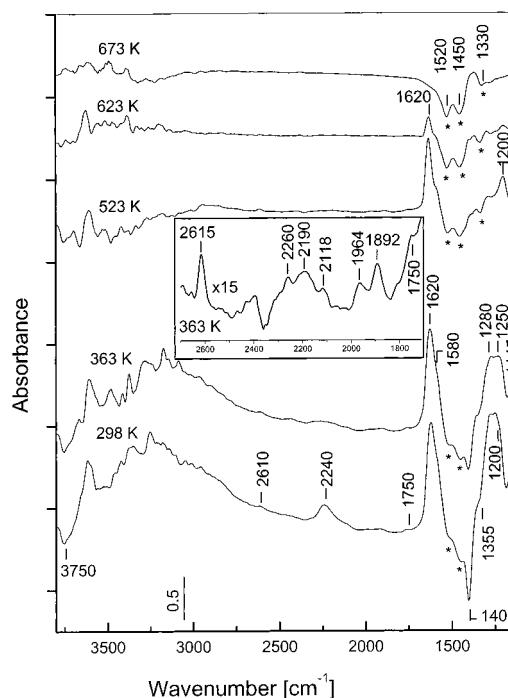
**Coadsorption of NO and O<sub>2</sub> at Room Temperature on Sulfated Zirconia.** The addition of 4.27 kPa of oxygen (Figure 10, spectrum b) to the IR cell containing NO (2.0 kPa) for 30 min (spectrum a in the same figure) causes a significant enhancement of the absorption bands in the whole region. The strong absorption in the 1650–1500 and 1355–1200 cm<sup>–1</sup> regions arises from nitrate species analogous to those formed during NO/O<sub>2</sub> coadsorption on pure zirconia. However, their amount is considerably smaller than in the Z sample (compare spectra b in Figures 6 and 10). This gives rise to very weak bands in the combination region of the nitrates.

Upon contact of the ZS sample with NO/O<sub>2</sub> mixture, the band at 1680 cm<sup>–1</sup> due to adsorbed HNO<sub>2</sub> disappears (Figure 10, spectrum b). The negative band in the OH-stretching region

broadens, indicating that additional  $\text{Zr}^{4+}\text{--OH}$  groups are involved in the adsorption process. Two strong bands with maxima at 3570 and 3380  $\text{cm}^{-1}$  are detected, which are attributed to  $\nu_{\text{as}}(\text{OH})$  and  $\nu_{\text{s}}(\text{OH})$  modes, respectively, of adsorbed water molecules, produced according to the process already described for the Z sample (see reaction 2). The  $\delta(\text{H}_2\text{O})$  mode falls in the region of the strong nitrate band at 1620  $\text{cm}^{-1}$ . The intensity of the negative band at 1400  $\text{cm}^{-1}$  (due to altered  $\text{SO}_4^{2-}$  groups during NO adsorption) has also increased. This can be explained by assuming a perturbation of some of the original sulfate groups caused by the  $\text{NO}_3^-$  species formed. The electronegative nitrate species affect the topmost  $\text{SO}_4^{2-}$  groups through an induction effect, which causes a shift of the band due to the  $\nu(\text{S=O})$  mode to lower frequency (a positive absorption at approximately 1355  $\text{cm}^{-1}$ , more clearly visible in spectrum c obtained after evacuation).

The broad absorption with a maximum at 1930  $\text{cm}^{-1}$  (Figure 10, spectrum b) can be attributed to adsorbed  $\text{N}_2\text{O}_3$  as in the case of the Z sample. The band at 2240  $\text{cm}^{-1}$  broadens and shifts to 2228  $\text{cm}^{-1}$ . It can be proposed that the latter absorption is due to the superimposition of bands associated with adsorbed  $\text{N}_2\text{O}$  and combination modes of the nitrate species. After evacuation for 15 min at room temperature (Figure 10, spectrum c), a band positioned at 2240  $\text{cm}^{-1}$  is detected again. This absorption is assigned to a residual amount of  $\text{N}_2\text{O}$  and combination mode of  $\text{NO}_3^-$  species. The weak band at 1750  $\text{cm}^{-1}$  (Figure 10, spectra b and c) is also due to a combination mode. Evacuation causes the disappearance of the band at 1930  $\text{cm}^{-1}$  assigned to adsorbed  $\text{N}_2\text{O}_3$ . This is accompanied by the loss of intensity and narrowing of the complex band at 1650–1500  $\text{cm}^{-1}$ , which indicates that the low-frequency shoulder at about 1530  $\text{cm}^{-1}$  is associated with  $\text{N}_2\text{O}_3$  [ $\nu_{\text{as}}(\text{NO}_2)$  mode<sup>24</sup>]. The band at 1120  $\text{cm}^{-1}$  due to water-perturbed sulfate groups shifts to 1145  $\text{cm}^{-1}$  after addition of oxygen and does not change significantly in intensity after evacuation at room temperature. The  $\nu_{\text{s}}(\text{NO}_2)$  mode of the nitrate species should appear between 1100 and 1000  $\text{cm}^{-1}$  but is not observed because of the enhancement of the absorption in this region after the admission of oxygen.

Heating the sample at 363 K in a vacuum (Figure 11) results in a small decrease in intensity of the nitrate bands and the almost complete disappearance of the band at 2240  $\text{cm}^{-1}$ . As shown above, a similar absorption arises from a combination between the  $\nu_{\text{as}}(\text{NO}_2)$  mode of the nitrates (at approximately 1250  $\text{cm}^{-1}$ ) and the corresponding vibrations due to the  $\nu_{\text{s}}(\text{NO}_2)$  mode. However, after evacuation at 363 K, the absorption at 1280–1250  $\text{cm}^{-1}$  decreases in intensity by less than 50%, whereas the decrease in intensity of the band at 2240  $\text{cm}^{-1}$  is approximately 10-fold (see the inset in Figure 11). This result confirms the suggestion that the absorption at 2240  $\text{cm}^{-1}$  is due mainly to strongly held  $\text{N}_2\text{O}$ , which desorbs or decomposes after heating at 363 K. The intensities of the bands at 1280 and 1145  $\text{cm}^{-1}$  and that of the negative band at 1400  $\text{cm}^{-1}$  decrease, which indicates that restoration of the perturbed sulfate groups has occurred. Heating under a vacuum at 523 K causes a decrease in intensity of the band at 1620  $\text{cm}^{-1}$ , which is accompanied by the disappearance of the hydrogen-bonded OH groups in the 3500–2750  $\text{cm}^{-1}$  region. This behavior is consistent with the suggestion that the band at 1620  $\text{cm}^{-1}$  is due to nitrate species and adsorbed water molecules. It seems that the bands at 1280 and 1145  $\text{cm}^{-1}$  are not present after this treatment and the sulfate groups are almost completely restored. However, because of the appearance of negative bands at 1520, 1450, and 1330  $\text{cm}^{-1}$  (indicated by asterisks) corresponding to



**Figure 11.** FTIR spectra obtained after heating of sample ZS containing preadsorbed  $\text{NO}_x$  species for 15 min in a vacuum at various temperatures. This spectrum (298 K) corresponds spectrum c in Figure 10.

residual carbonate species (see Figure 1, spectrum ZS) that undergo decomposition during the vacuum heat treatment, it is difficult to follow the behavior of the band at 1400  $\text{cm}^{-1}$ . Evacuation at 673 K causes complete desorption of the nitrate species and restoration of the original hydroxyl groups.

The inset in Figure 11 shows the combination region of the fundamental nitrate bands in the spectrum obtained after evacuation at 363 K. As illustrated above, the bands in the combination region can help in determining the type of coordination of surface nitrates. The presence of a relatively symmetric band at 2615  $\text{cm}^{-1}$  indicates that there is only one type of bidentate  $\text{NO}_3^-$  species with the fundamental band at 1580  $\text{cm}^{-1}$  [ $\nu(\text{N=O})$  mode]. Taking into account that the former band represents a sum of the  $\nu(\text{N=O})$  and  $\nu_{\text{s}}(\text{NO}_2)$  modes of bidentate nitrates, the position of their  $\nu_{\text{s}}(\text{NO}_2)$  vibration can be estimated as approximately 1040–1050  $\text{cm}^{-1}$ . The poorly resolved band at 1750  $\text{cm}^{-1}$  also confirms the existence of bidentate nitrates. The pair of bands at 1964 and 1892  $\text{cm}^{-1}$  supports the presence of bridged  $\text{NO}_3^-$  species (fundamental band at 1620  $\text{cm}^{-1}$ ). The absorption at 2260  $\text{cm}^{-1}$  corresponds to a binary combination between the  $\nu_{\text{as}}(\text{NO}_2)$  mode at 1200  $\text{cm}^{-1}$  and  $\nu_{\text{s}}(\text{NO}_2)$  vibration (estimated at approximately 1080  $\text{cm}^{-1}$ ) of the bridged nitrates. The band at 2118  $\text{cm}^{-1}$  probably is associated with a combination between the component at 1145  $\text{cm}^{-1}$  of the split  $\nu_3$  mode and the  $\nu_1$  mode of the perturbed sulfate groups. The latter vibration is at approximately 990  $\text{cm}^{-1}$ ,<sup>21</sup> and it was not observed by us. By using the estimated values of  $\nu_{\text{s}}(\text{NO}_2)$  modes of the nitrate species, the band at 2190  $\text{cm}^{-1}$  could be interpreted as a sum between the  $\nu_{\text{s}}(\text{NO}_2)$  mode of nitrate and the  $\nu_3$  component at 1145  $\text{cm}^{-1}$  of sulfato species. The first overtone of the band at 1250  $\text{cm}^{-1}$  due to nitrate species should appear between 2500 and 2400  $\text{cm}^{-1}$ . However, the absorption in this region is very weak and obscured by the negative band due to ambient  $\text{CO}_2$  and, therefore, cannot be used in the assignment.

On the basis of these considerations, the nitrate species formed upon  $\text{NO}/\text{O}_2$  coadsorption on the ZS sample are identified as

**TABLE 2: Assignments of the FTIR Bands Observed during Adsorption of 1.07 KPa of NO and Its Coadsorption with O<sub>2</sub> (NO:O<sub>2</sub> = 1:2) at Room Temperature on Sulfated Zirconia**

| NO <sub>x</sub> species                               | band positions (cm <sup>–1</sup> ) | modes                                                                                                                                                        |
|-------------------------------------------------------|------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|
| N <sub>2</sub> O (ads)                                | 2290, 2240<br>1230                 | $\nu(\text{NN})$<br>$\nu(\text{NO})$                                                                                                                         |
| Zr <sup>4+</sup> –NO                                  | 1912                               | $\nu(\text{NO})$                                                                                                                                             |
| ON–Zr <sup>4+</sup> –(SO <sub>4</sub> <sup>2–</sup> ) | 1950–1960                          | $\nu(\text{NO})$                                                                                                                                             |
| N <sub>2</sub> O <sub>3</sub>                         | 1930<br>1530                       | $\nu(\text{N=O})$<br>$\nu_{\text{as}}(\text{NO}_2)$                                                                                                          |
| cis-HNO <sub>2</sub> (ads)                            | 1680                               | $\nu(\text{N=O})$                                                                                                                                            |
| H <sub>2</sub> O (ads)                                | 3550–3000<br>1610                  | $\nu(\text{OH})$<br>$\delta(\text{HOH})$                                                                                                                     |
| NO <sub>3</sub> <sup>–</sup> (bridged)                | 1620<br>1200                       | $\nu(\text{N=O})$<br>$\nu_{\text{as}}(\text{NO}_2)$                                                                                                          |
|                                                       | 2260                               | $\nu_{\text{as}}(\text{NO}_2) + \nu_{\text{s}}(\text{NO}_2)$                                                                                                 |
|                                                       | 1964, 1892                         | $\nu_{\text{s}}(\text{NO}_2) + \delta(\text{ONO})$                                                                                                           |
| NO <sub>3</sub> <sup>–</sup> (bidentate)              | 1580<br>1250<br>2615<br>1750       | $\nu(\text{N=O})$<br>$\nu_{\text{as}}(\text{NO}_2)$<br>$\nu(\text{N=O}) + \nu_{\text{s}}(\text{NO}_2)$<br>$\nu_{\text{s}}(\text{NO}_2) + \delta(\text{ONO})$ |

bridged (1620 and 1200 cm<sup>–1</sup>) and bidentate (1580 and 1250 cm<sup>–1</sup>) nitrates.

Table 2 illustrates the absorption bands observed during NO adsorption and its coadsorption with O<sub>2</sub> on sulfated zirconia.

## Conclusions

The adsorption of NO at room temperature on pure and sulfated zirconia occurs through disproportionation, leading to the formation of nitrous acid; water molecules; nitro species; and anionic nitrosyls, NO<sup>–</sup>. The latter species are stable on the surface of zirconia, whereas, on the sulfated sample, they are readily oxidized by the SO<sub>4</sub><sup>2–</sup> groups. The process of NO disproportionation is favored by wet surfaces and occurs with the participation of the hydroxyl groups of zirconia. These are tribridged OH groups for pure zirconia and terminal OH groups for sulfated sample. The anionic nitrosyls are stable in an oxygen atmosphere at room temperature but are oxidized at 573 K. If they are in contact with a NO/O<sub>2</sub> mixture at room temperature they transform into nitrate species.

The coadsorption of NO and O<sub>2</sub> on pure zirconia leads to the formation of monodentate, bidentate, and bridged nitrate species. On sulfated zirconia, no monodentate NO<sub>3</sub><sup>–</sup> species are formed, and the total surface concentration of the NO<sub>3</sub><sup>–</sup> ions is lower. In addition, the nitrate species obtained on the sulfated zirconia are thermally less stable than those on pure zirconia.

Analysis of the combination bands of the nitrate species shows that this spectral region can be used for the structural identification of bidentate and bridged nitrates. Bridged nitrates produce combination bands at 2845–2800 cm<sup>–1</sup> and a pair of bands at 1980–1960 and 1900–1890 cm<sup>–1</sup>. Bidentate nitrates can be distinguished by the appearance of combination bands in the region of 2600 cm<sup>–1</sup> and a pair of bands at 1755 and 1700 cm<sup>–1</sup>.

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