

INFRARED STUDY OF NITRIC OXIDE (NO) ADSORPTION AND CONVERSION ON CeO₂-ZrO₂ MIXED OXIDE

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An IR study of adsorption of NO- and CO-containing mixtures on a high-surface-area Rh/Ce_{0.5}Zr_{0.5}O₂ mixed oxide is reported. At low temperatures, NO strongly interacts with surface oxygen. The presence of various NO_x-containing species co-ordinated both to cerium and zirconium has been observed. The NO_x storage capacity is mainly associated with the presence of zirconium sites. The extension of NO_x storage capacity strongly depends on the adsorption temperature, which is associated with the presence/absence of reactive surface oxygen species. Formation of N₂O₂²⁻ as adsorbed species appears to be a possible key step in the mechanism for conversion of NO at low temperature.

Keywords: Nitric oxide; Adsorption; Conversion; CeO₂-ZrO₂; Mixed oxides; Zirconium; Cerium; Catalytic removal of NO; IR spectroscopy; Heterogeneous catalysis.

The catalytic removal of NO_x from the exhaust stream of cars is still an important and challenging task. In fact, although today's three-way catalysts show good performances, their activity at low temperature (cold start) is still too poor. Moreover, despite intensive research in the field of the so-called lean-DeNO_x catalysts^{1,2}, *i.e.* NO_x conversion catalysts able to reduce NO_x to N₂ under excess of oxygen, no sufficiently active catalyst has been developed so far, which would attain the standard for NO_x emission beyond 2 005 for, for example, light-duty diesel-engine vehicles. In our investigations of new three-way catalyst formulations, we have shown that ceria-zirconia mixed oxides, in addition to having a high oxygen storage capacity³, also exhibit promising results for NO conversion at low temperature⁴⁻⁷. We have suggested that while at high temperature, the noble metal is the active site for conversion of NO, below 500 K, Ce-containing support is involved in the reduction of NO (refs^{4,6}). We have therefore extended our study to an investigation by IR spectroscopy of the interaction of NO with CeO₂-ZrO₂ mixed oxide with the aim of understanding the role of this system in NO_x conversion, as well as its NO_x storage capacity.

EXPERIMENTAL

The Rh/Ce_{0.5}Zr_{0.5}O₂ sample was from a previous study⁶. The nominal Rh loading is 0.5%. Approximately 18 mg of the powder was pressed (10 Kp cm⁻²) into a wafer of 2 cm², mounted in a wafer holder and loaded into an *in situ* IR flow-cell. The heating system allowed the sample to be heated up to 773 K, as measured by a thermocouple which abuts the sample. Selected experiments were also carried out in a quartz static cell, where it was possible to get a vacuum of about $1.33 \cdot 10^{-2}$ Pa and heat the sample up to 1 127 K. In both cases, CaF₂ windows were used. The spectra were collected either at room temperature (static cell) or at the reaction temperature (flow cell) on a Perkin-Elmer 2000 Fourier-Transformer spectrometer using a MCT detector. The resolution was 4 cm⁻¹ and the reported spectra are an average of 64 scans. The spectra were treated with the help of the GRAMS ResearchTM software.

Before introducing the reaction mixture, the catalyst was pre-treated in Ar (20 ml min⁻¹) at 773 K for 5 h and then activated in H₂ flow (20 ml min⁻¹) at 473 K for 2 h. The *in situ* experiments were carried out under a total flow of 20 ml min⁻¹ of 1.4% CO and/or 1.4% NO in He.

RESULTS AND DISCUSSION

Before addressing the results of the present investigation it is important to shortly recall some relevant data obtained in the investigation of the catalytic activity in the reduction of NO with CO using the present catalyst. It is well known that Rh is the metal of choice which effectively promotes NO reduction under exhaust conditions. This was associated with its ability to dissociate NO (ref.⁸). However, at low temperatures (300–500 K) the Rh catalysts are not very active and generally present two kinetic regimes characterised by distinct activation energies^{9,10}. This was associated with the occurrence of the well-known Rh reductive agglomeration-oxidative disruption phenomenon¹¹, leading to different Rh morphology on the Al₂O₃ surface, depending on the reaction temperature¹². By using a Ce_{0.5}Zr_{0.5}O₂ mixed oxides as a Rh support, we have observed that there is a remarkably high activity of the catalyst below 500 K, which is reversibly deactivated by increasing the reaction temperature above 500 K. This results in a conversion vs temperature curve featuring a local maximum of activity around 500 K in the NO conversion as exemplified in Fig. 1 (ref.⁶). Typically, apparent activation energies of about 15 and 30 kcal mol⁻¹ were observed respectively below and above 500 K. The origin of this catalytic behaviour is therefore addressed here by investigating the nature and transformation of surface adsorbed species under the reaction conditions at 473 and 523 K using the IR technique. These temperatures are representative of the two kinetic regimes observed under the reaction conditions.

In order to correlate the *in situ* IR data with the results from the previous catalytic experiments⁶, we decided to mimic those conditions. Therefore a similar standard cleaning procedure, consisting in flowing Ar at 773 K for 5 h, has been adopted. It is worth noting that the cleaning pre-treatment removes water adsorbed on the surface of the sample but influences only slightly the OH groups of the sample. A significant decrease of the bands of the hydroxy groups is observed only in vacuum above 573 K. More strongly affected is the 1 650–1 200 cm^{-1} region, where the bands due to various type of carbonates^{13–15} are present. Note, however, that several other adsorbed species were detected at the surface of CeO_2 depending on the pre-treatment¹⁶. In fact, significant decrease of all the bands in the 1 650–1 200 cm^{-1} region is observed during the adopted pre-treatment. Strongly bound carbonates (polydentates and didentates) are not easily removed and only more efficient cleaning procedures, like heating in dilute oxygen¹⁷ ensure the elimination of carbonate impurities from the CeO_2 – ZrO_2 surfaces.

CO Adsorption on $\text{Rh}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$

The interaction of CO with CeO_2 and ZrO_2 is well documented in the literature^{13,15,18–20}, and the formation of various types carbonates and other spe-

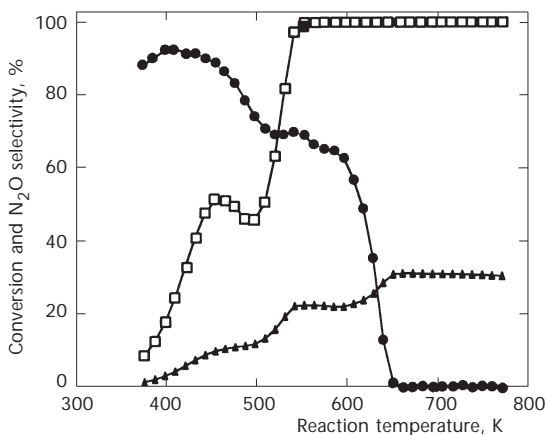


FIG. 1

Reduction of NO with CO over $\text{Rh}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$: reaction profile vs temperature (reaction conditions: NO 1% and CO 3% in He, heating/cooling rate 1 K min^{-1} , $W/F = 1 \cdot 10^{-3} \text{ g}_{\text{cat}} \text{ ml}^{-1} \text{ min}$). Selectivity in N_2O formation (●), CO conversion (▲) and NO conversion (□)

cies are reported. Figures 2 and 3 report IR spectra obtained upon adsorption of CO over Rh/Ce_{0.5}Zr_{0.5}O₂ under static and dynamic conditions, respectively. Under static conditions, two broad adsorption bands at about 1 600 and 1 330 cm⁻¹ are apparent, in addition to weak adsorption bands at 1 160 and 1 060 cm⁻¹ and a shoulder at 1 690 cm⁻¹. In addition, bands due to gaseous CO can be seen above 2 000 cm⁻¹. The very broad pattern of the bands at 1 700–1 300 cm⁻¹ does not allow an unequivocal attribution, different carbonate or carboxylate species possibly being at the origin of these bands. However, it should be recalled that CO is primarily adsorbed without further reaction over ZrO₂ (ref.¹⁸). Therefore, the CeO₂ component plays a key role in providing the oxygen species leading to CO fixation (oxidation) at the surface. The intensity of these bands is relatively

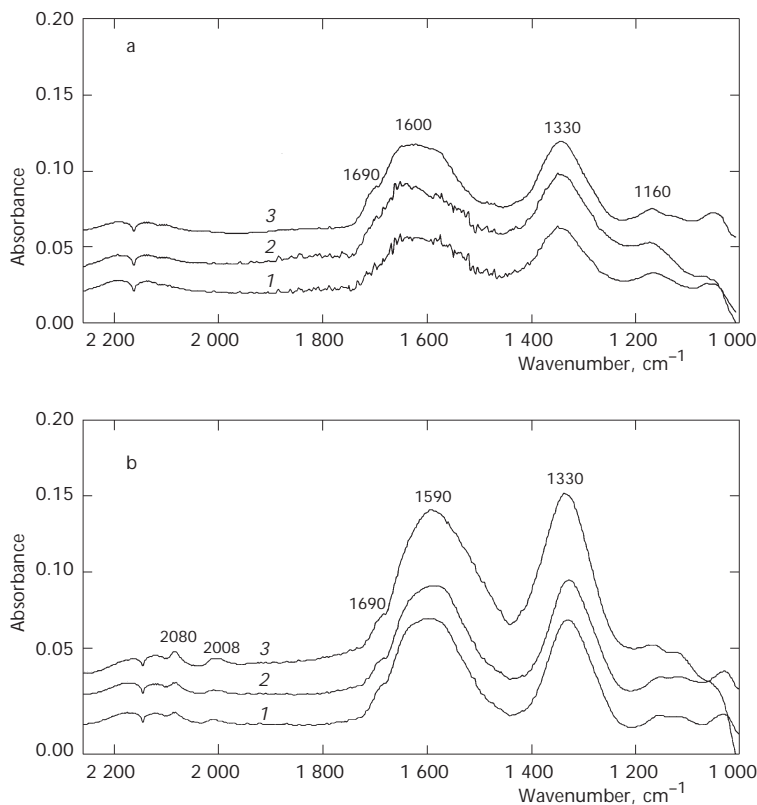


FIG. 2

CO adsorption ($P_{\text{CO}} = 1.33$ kPa) on Rh/Ce_{0.5}Zr_{0.5}O₂ at 473 K (a) for reaction times 30 min (1), 3 h (2), 18 h (3), and 523 K (b) for reaction times 30 min (1), 90 min (2), and 4 h (3)

low but it increases when the sample was pre-oxidised before CO adsorption (Fig. 3).

At 523 K, geminal-dicarbonyl CO species adsorbed on Rh ($2\ 080$ and $2\ 008\text{ cm}^{-1}$) are discernible even after 4 h, indicating that reductive agglomeration of Rh dicarbonyl species did not occur. As shown in Fig. 3, this was confirmed also under flow conditions where, due to a higher amount of CO passed over the catalyst, Rh geminal-dicarbonyl is observed at both reaction temperatures investigated. This is an important observation since under similar reaction conditions dispersed Rh/Al₂O₃ geminal-dicarbonyl species quickly agglomerated, even in the presence of NO which makes reductive

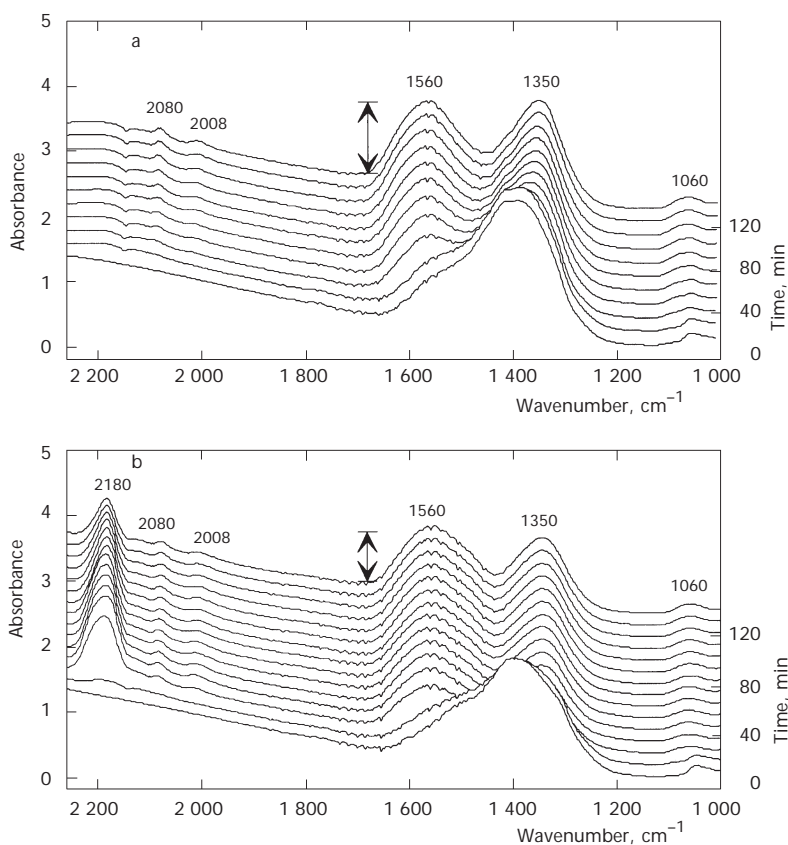


FIG. 3

CO adsorption vs time on Rh/Ce_{0.5}Zr_{0.5}O₂ under flow conditions at 473 (a) and 523 K (b). Catalyst pretreated in flow of NO at the same temperature

agglomeration difficult^{12,21}. This rules out that a change of the Rh dispersion upon variation of the reaction temperature is at the core of the above commented catalytic activity. This also confirms the ability of CeO₂ containing materials to favour and stabilise noble metal dispersion¹⁶.

CO adsorption both at 473 and 523 K was also investigated under flow conditions (Fig. 3). In this case, the catalyst was pre-treated in NO (as indicated by the broad adsorption at approximately 1 400 cm⁻¹) before the experiment. It is observed that the NO-derived species are slowly replaced by CO-derived species. At comparable reaction times, the intensity of the bands at 1 600–1 300 cm⁻¹ is significantly higher for adsorption temperature of 473 K compared to 523 K. At 523 K, a band at 2 180 cm⁻¹ attributed to surface isocyanates^{22,23} is formed, whose intensity decays with reaction time.

NO Adsorption on Rh/Ce_{0.5}Zr_{0.5}O₂

Adsorption of NO at 473 K on prereduced Rh/Ce_{0.5}Zr_{0.5}O₂ leads to the spectrum reported in Fig. 4 (curve 1). A possible deconvolution of the broad band at 1 398 cm⁻¹ using a combination of Gaussian and Lorentzian functions is shown in the inset. A reasonable fit was obtained with five bands at

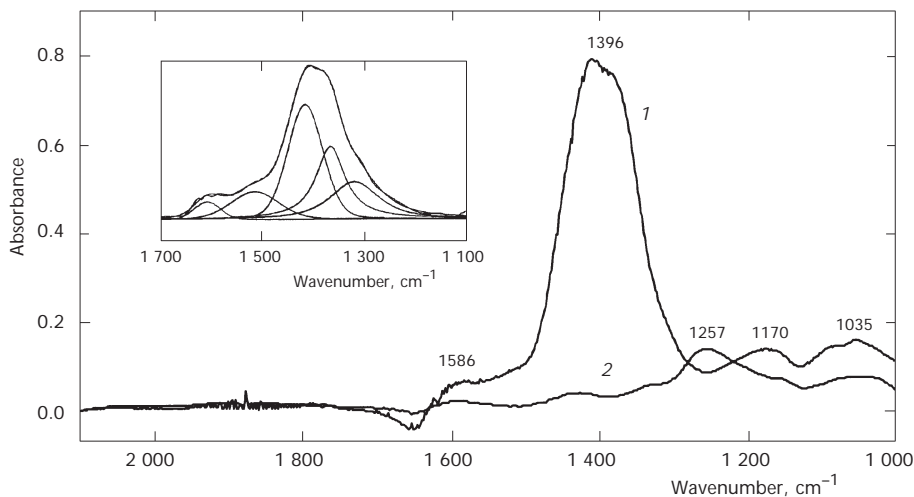


FIG. 4

NO adsorption (contact time 15 min, $P_{\text{NO}} = 1.33$ kPa) at 473 (1) and 523 K (2) over Rh/Ce_{0.5}Zr_{0.5}O₂ pre-reduced at the same temperatures. Inset: Deconvolution of the peak at about 1 400 cm⁻¹ obtained on a sample degassed at 473 K

1 607, 1 514, 1 415, 1 367 and 1 320 cm^{-1} . The broadness of the peak and the fact that the spectrum somewhat changes with time and pretreatment at 473 K make an unambiguous assignment difficult. However, even if slightly displaced²⁴, attribution of the bands at 1 514 and 1 415 cm^{-1} , respectively, to ν_{asym} and ν_{sym} of surface monodentate nitrates co-ordinated to ZrO_2 appears highly reasonable; the relative intensity of these bands²⁵ further supporting this assignment. The presence of different possible adsorption sites due to the different crystal habit of ZrO_2 (cubic compared to tetragonal or monoclinic previously reported) could easily account for the band shift. Notice that some contribution from surface carbonates, *e.g.* bands at 1 607 and 1 367 cm^{-1} , to the broad adsorption centred at 1 396 cm^{-1} cannot be discounted. Such species could be formed by interaction of occluded carbon-containing species with reactive oxygen species²⁰, the latter being generated by the disproportionation of NO. Noticeably, of all NO derived species which could be formed at CeO_2 surface sites²⁶, only a surface nitrates feature a band above 1 350 cm^{-1} (1 505 cm^{-1}) fully supporting the attribution of the broad adsorption band to co-ordination of NO-derived species to primarily zirconia sites. In fact, the band at 1 320 cm^{-1} is consistent with the presence of nitrites co-ordinated to zirconia²⁴.

The band at 1 035 cm^{-1} is possibly associated with hyponitrite species at the ceria centres²⁴⁻²⁸. Note that the latter species is considered to be a precursor for N_2 and N_2O formation over reduced ceria sites^{26,27}. The band at 1 170 cm^{-1} can be associated with a chelating nitrite species on a cerium site, the stretching at higher wavenumbers being overlaid on the band at 1 398 cm^{-1} (ref.²⁶). The overall picture clearly shows that upon adsorption of NO on the reduced surface at 473 K, a rapid reaction occurs with significant NO_x storage under oxidised forms and simultaneous NO reduction. Consistently, N_2O , also in the gas phase, was detected by bands at 2 234 and 2 217 cm^{-1} (data not reported).

A remarkably different reactivity is observed when the adsorption of NO is carried out at 523 K. At equal contact time only a weak band at 1 257 cm^{-1} is observed which can be safely associated with the presence of adsorbed N_2O generated by a redox reaction of the reduced support with NO. As above, N_2O , also in the gas phase, was detected by bands at 2 234 and 2 217 cm^{-1} (data not reported), even though their intensity was somewhat smaller. Even though the presence of some surface NO^- or chelating nitrite species over cerium sites (compare the weak shoulder at about 1 160 cm^{-1}) cannot be discounted²⁶, the overall picture strongly suggests that, at 523 K, NO activation occurs essentially by a redox reaction at the reduced Ce^{3+} sites, which results in filling the oxygen vacancies created by the reduction and

generating N_2O . We believe that, as previously suggested^{29,30}, oxygen vacancies, which are located in the bulk of the mixed oxide, provide the driving force for the redox reaction, the formation of surface oxygen species generated by the NO disproportionation being relatively inhibited. As a consequence, no migration of adsorbed NO-derived species towards zirconium sites is evidenced within the time scale shown in Fig. 4. The poorer ability of this sample to interact with NO is also documented by a lower intensity of the above mentioned N_2O derived bands compared to the sample treated at 473 K.

To check whether a lack of reactive surface oxygen species was responsible for the decreased ability of the mixed oxide to store NO_x , NO_x adsorption with time was monitored over prerduced and preoxidised sample at 473 and 523 K (Figs 5 and 6). In all cases, a similar type of reaction profiles

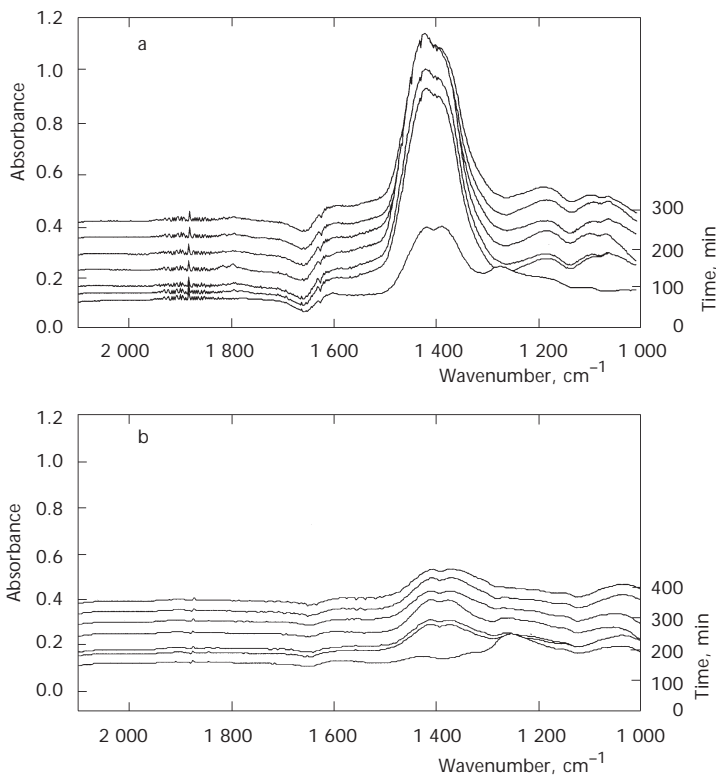


FIG. 5

Time resolved IR spectra of NO adsorption under static conditions ($P_{\text{NO}} = 1.33$ kPa) at 473 (a) and 523 K (b) carried out over $\text{Rh}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ prerduced (2 h) at the same temperatures

is obtained, however, the reactions leading to the accumulation of surface NO_x species occur more rapidly at 473 K. Significantly, the intensity of the broad band at about $1\,400\text{ cm}^{-1}$ is higher at the lower adsorption temperature (473 K) and in the presence of surface oxygen species. This is consistent with the ability of surface oxygen to promote NO oxidation to surface “nitrite/nitrate” species, which are effectively stored in these forms at support zirconia sites, acting as accumulation sites in the lean- NO_x storage/reduction concept³¹. However, the observation that NO_x storage is depleted by increasing the reaction temperature from 473 to 523 K is an indication that cerium sites act as an intermediate under our reaction conditions where NO is reduced, thereby generating reactive oxygen species which

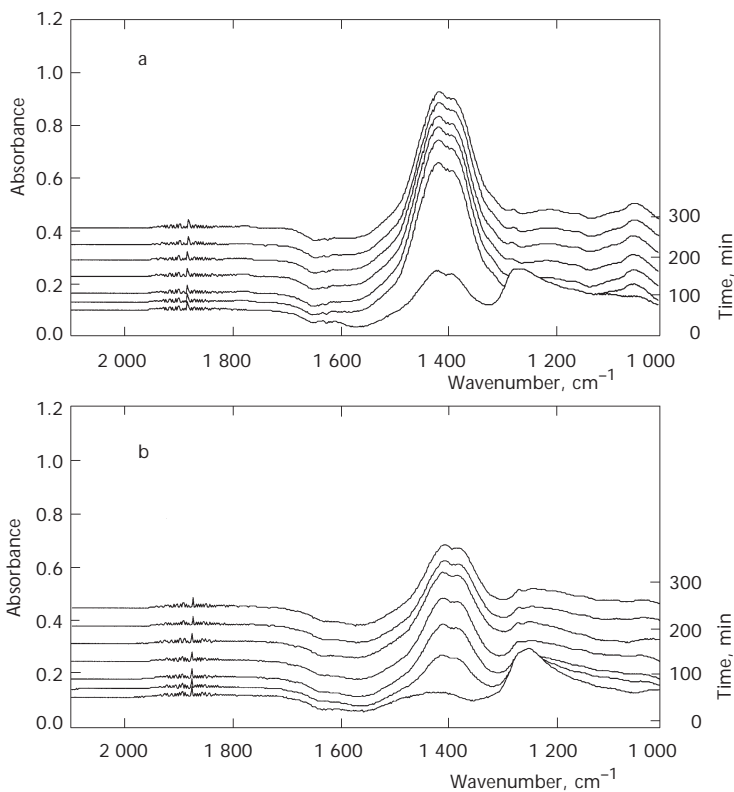


FIG. 6

Time resolved IR spectra of NO adsorption under static conditions ($P_{\text{NO}} = 1.33\text{ kPa}$) at 473 (a) and 523 K (b) carried out over $\text{Rh/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ preoxidised (5 min) at the same temperatures

promote oxidation of adsorbed NO to adsorbed nitrite. Migration of such species to ZrO₂ then provides a way to achieve NO_x storage on the support.

The lower ability of the system to store NO_x species on the support at 523 K should be associated with desorption/loss of active surface oxygen species at the ceria sites with increasing temperature. Consistently, highly dispersed CeO₂ easily loses oxygen upon heating and evacuation³². A decreased stability of the nitrite/nitrate species at 523 K compared to 473 K should not be at the origin of the different reactivity observed. In fact, as exemplified in Fig. 7 for the NO_x species generated by adsorption at 523 K, significant desorption, as documented by the broad negative band centred at 1 400 cm⁻¹, was observed after the experiment depicted in Fig. 6b only at 623 K. At lower temperatures only some interconversion of the adsorbed NO_x species occurred. This results is consistent with those reported by Ghiotti and Prinetto who found that NO_x storage over ZrO₂ increased with temperature²⁴.

CONCLUSIONS

This IR study indicates that the adsorption, reduction and storage of NO on the CeO₂-ZrO₂ mixed oxide is a facile process at low temperatures. Ceria plays a crucial role in that, NO is rapidly disproportionated at reduced ceria

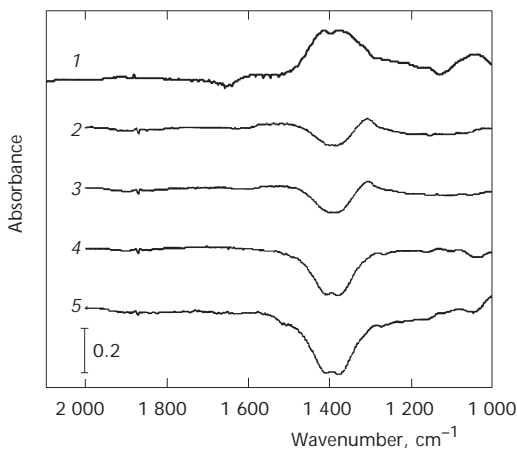


FIG. 7

Desorption of surface NO_x species generated by NO adsorption at 523 K for 300 min: initial spectrum (1); difference spectra obtained by subtracting the spectrum obtained after evacuation ($6 \cdot 10^{-2}$ Pa) for 3 h at 473 (2), 523 (3), 623 (4) and 823 K (5) from initial spectrum

sites, generating active oxygen species. These species further react with NO to generate adsorbed nitrites/nitrates. The NO_x storage capacity of the system is mainly associated with the stability of nitrates and nitrites on zirconium, migration of such species from ceria to zirconia being the mechanism for NO_x storage. Finally, in the presence of CO, conversion of NO can occur at low temperatures in a CeO₂-ZrO₂ mediated mechanism which involves the decomposition of hyponitrites to both N₂O and N₂.

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