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Elementary steps of NO_x adsorption and surface reaction on a commercial storage–reduction catalyst

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Abstract

The surface species formed during adsorption of NO_x on a commercial NSR catalyst (containing barium oxide, Pt, and alumina as the main components) were investigated by in situ IR spectroscopy. During adsorption of NO, mainly linear and bridged bonded nitrites of Ba–O–N–O–Ba type were formed on Al and Ba oxide components. Nitrites were detected during the initial phase of the NO/O_2 and NO_2 adsorption, whereas with further exposure nitrates were the dominant surface species. Using the different surface species and reaction intermediates identified by IR spectroscopy a series of sequential reaction steps during the sorption of NO_x on a NSR catalyst was derived. Initially, NO is stored in the form of nitrites on the storage component (Ba oxide). NO_2 formed by oxidation on the noble metal component (Pt) sorbs either molecularly by forming nitrate species or dissociatively by forming nitrites. After a certain concentration of NO_x is adsorbed, the transformation and further oxidation of the surface nitrites into surface nitrates by NO_2 occur. The stability of the NO_x surface species was found to increase in the order Al nitrites < Ba nitrites < Al nitrates < Ba nitrates.

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Keywords: Nitrates; Nitrites; In situ FTIR spectroscopy; NO_x storage; Adsorption; Barium-oxide; Mechanism

1. Introduction

Conventional Pt–Rh-based three-way catalysts (TWCs) are very efficient in reducing nitrogen oxide (NO_x), CO, and unburned hydrocarbon (HC) emissions from gasoline engines. However, the general demand for lower CO_2 emissions and, thus, the requirement of more fuel-efficient gasoline engines led to the development of lean-burn engines operating at significantly higher air-to-fuel ratios then used by traditional engines [1]. Under these oxygen-rich exhaust-gas conditions three-way catalysts cannot efficiently reduce NO_x. The most promising approach to the reduction of NO_x under lean-burn conditions is based on the concept of NO_x storage-reduction (NSR), where the engine is operated in a mixed lean/rich operation mode [2,3]. NSR catalysts contain storage components, typically alkali or alkaline earth metals, such as barium, and noble metal components providing oxidation/reduction functionality. Under lean operation conditions (i.e., oxidizing atmosphere), NO is oxidized to NO_2 over the noble metal component and stored on the storage component. By periodic changes to short cycles of rich operating conditions (i.e., reducing atmosphere), NO_2 is released from the storage component and converted to N_2 over the metal component. The major drawback of this process at present is the high susceptibility of the NSR catalysts to sulfur poisoning, which lowers the NO_x storage capacity [4,5].

A detailed understanding of the overall NO_x storage mechanism is one of the basic steps required to improve the efficiency, as well as the sulfur resistance, of the catalysts. Several studies have focused recently on the mechanism of NO_x storage on model NSR catalysts [5–11]. In an early study, Takahashi et al. [5] investigated commercial NSR catalysts and found indications of oxidation of NO on metal sites and subsequent storage on adjacent storage sites in the form of nitrates. Mahzoul et al. [8] suggested that two different Pt sites are involved in the storage process, one close to BaO related to the nitrate formation and another (further away) acting as oxidation catalysts for NO. The authors also reported the formation of nitrates in the absence of gas phase oxygen and in the absence of Pt.

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Fridell et al. [10] suggested two possible reaction pathways for NO_x storage with NO_2 as the primary oxidizing agent during NO_x storage. The first proposed reaction path includes the oxidation of BaO to BaO_2 by NO_2, whereas the second pathway proposed involves the initial formation of nitrites with subsequent oxidation to nitrates by NO_2. In more detail, Prinetto et al. [11], as well as Westerberg et al. [6], studied the interaction of NO and NO_2 in the presence of O_2 with model storage catalysts such as $Pt/BaO/Al_2O_3$ by IR spectroscopy. The main surface species observed were hyponitrites, nitrites, and nitrates on alumina and Ba oxide. Furthermore, Westerberg et al. [6] proposed that Al_2O_3 could play an important role as a storage site at temperatures below 300 °C.

As most of the studies were performed on model systems, detailed investigations of the NO_x storage mechanism on commercial NSR catalysts are required. The purpose of the present study is to obtain an improved understanding of the NO_x storage mechanism by identifying the surface species and reaction intermediates on such a catalyst under reaction conditions closely related to the practical application conditions. The catalyst was exposed to different gas compositions typical of the NSR process (i.e., NO, NO/O_2, and NO_2), and the NO_x species formed on the catalyst surface were investigated by in situ IR spectroscopy, leading to a sequence of reaction steps for the NO_x storage process.

2. Experimental

The catalyst studied in this work was a commercial NO_x storage–reduction catalyst containing $\sim$ 1 wt% noble metals (Pt and Rh) as oxidation/reduction component and $BaO/BaCO_3$ ($\sim$ 8 wt%) as storage component, deposited on an Al_2O_3 support. From EXAFS analysis of the fresh sample the dispersion of the Pt particles was estimated to be 95%. The specific surface area of the catalyst, determined by N_2 sorption (BET method), was 110 m^2/g.

XRD measurements were performed on a Rigaku powder diffractometer with Cu-K_α radiation. The tube voltage was 40 kV and the current was 40 mA. The XRD diffraction patterns were taken in the 2θ range of 10–90° at a scan speed of 2° per min at RT before and after the sample was heated in He to 700 °C.

The sorption experiments of the reactants were carried out in an IR flow cell (CaF_2 windows) using a gas-mixing unit controlled by electronic flow controllers used for the simultaneous admission of NO_2, NO, and O_2. The catalyst powder was pressed into thin self-supporting wafers ($\sim$ 5 mg) and analyzed in situ during all treatments by IR spectroscopy in the transmission absorption mode (resolution 4 cm^{-1}). The wafer was fixed in the middle of the IR cell in a heatable sample holder made of Au. For temperature control, a thermocouple was in direct contact with the sample holder. Further details of the experimental setup are described in Ref. [12].

Prior to each adsorption experiment the fresh catalyst was activated in He (flow 25 ml/min) at 550 °C for 60 min. After activation the catalysts were exposed to a gas stream containing 500 ppm NO, 500 ppm NO/5% O_2, and 500 ppm NO_2 in helium (total flow 25 ml/min) at 50 °C.

The thermal stability of the NO_x surface species formed on the catalyst after exposure to NO, NO/O_2 or NO_2 were investigated at temperatures between 50 and 550 °C with a temperature increment of 5 °C/min under constant He flow.

All spectra shown are difference spectra derived from the spectra of the catalyst in contact with the sorbents, from which the spectra of the catalyst after activation are substracted.

3. Results

3.1. Catalyst characterization

The XRD patterns of the fresh and activated catalyst are given in Fig. 1. Besides the reflections typical for the support [13], the XRD pattern of the catalyst before activation exhibited reflections characteristic for $BaCO_3$ at 2θ values of 24°, 24.3°, 34.1°, 34.7°, 42.1°, and 44.8° (indicated by $*$) and for BaO at 46.2° (indicated by $\bigcirc$). In the XRD pattern recorded after thermal treatment up to 700 °C the presence of $BaCO_3$ was observed at a much lower concentration. Characteristic peaks for additional

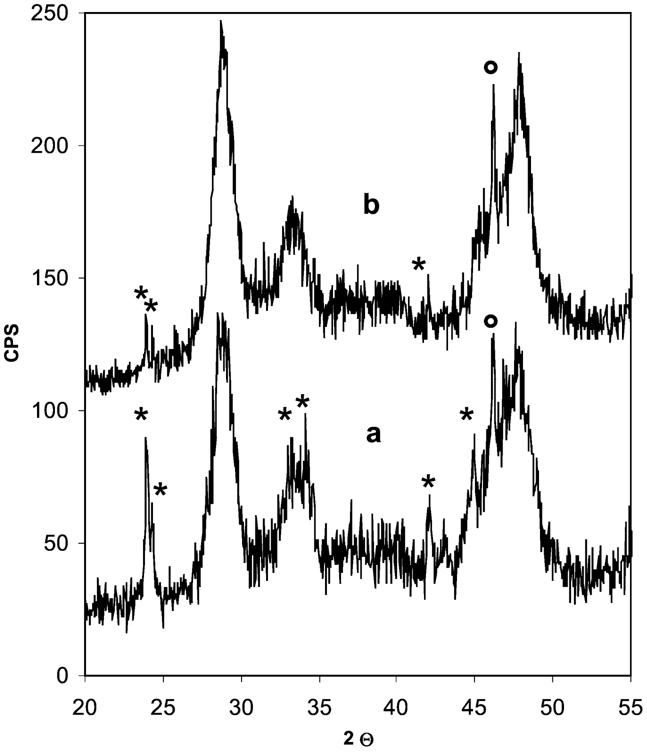


Fig. 1. XRD diffraction pattern for the catalyst (a) before and (b) after activation up to 700 °C in He. Both pattern were recorded at 50 °C. ($*$) $BaCO_3$; ($\bigcirc$) BaO.

Ba oxide species formed during the decomposition of the carbonates were not observed. This suggests that the Ba carbonates are transformed into highly dispersed or amorphous barium oxide species, which are not detectable by XRD. A crystalline phase of Pt was not observed, which indicates the presence of highly dispersed platinum particles.

IR spectra recorded during activation of the catalyst to 500 °C (not shown here) confirmed these observations. A broad band at 1450 cm^{-1} with shoulders at 1500, 1420, and 1367 cm^{-1} was observed on the fresh catalyst; it is assigned to Ba carbonates [14,15]. During activation a decrease in the intensity of this band indicated the partial decomposition of $BaCO_3$ at temperatures up to 500 °C. It should be noted, however, that the temperature observed for carbonate decomposition in these experiments was far below that typically required for the decomposition of bulk $BaCO_3$ (> 1000 °C) [16].

3.2. *IR spectroscopic study of the NO_x storage process*

3.2.1. *Exposure to NO*

IR spectra during exposure of the catalyst to 500 ppm NO at 50 °C are shown in Fig. 2. The sorbed species are attributed predominantly to nitrites affiliated with Ba- and Al-oxide. After 5 min of exposure a broad band was observed at 1206 cm^{-1}, together with weak bands at 1627 and 1569 cm^{-1} and two negative bands at 1456 and 1297 cm^{-1}. The negative bands result from the decomposition of Ba carbonates during NO sorption [14]. The weak bands at 1627 and 1569 cm^{-1} are assigned to nitrates on Al oxide sites forming bridging bidentate and chelating bidentate type species, respectively [6,11]. These species are expected to have further vibrational modes in the range from 1300 to 1200 cm^{-1} [17,18], which were overlapped by the negative band at 1297 cm^{-1} (carbonate decomposition) and the broad band at 1206 cm^{-1}, arising from the contributions of several NO_x species. Note that the formation of nitrates during NO exposure requires the oxidation of adsorbed NO with reactive oxygen species that are present on the catalyst surface. Besides the contribution assigned to bridged and chelating nitrates, the main component of the broad band at 1206 cm^{-1} is assigned to bridged bidentate nitrites, which are expected also to have a band at approximately 1300 cm^{-1} [11]. This band could not be clearly distinguished, which is attributed to its masking by the negative carbonate band in this region.

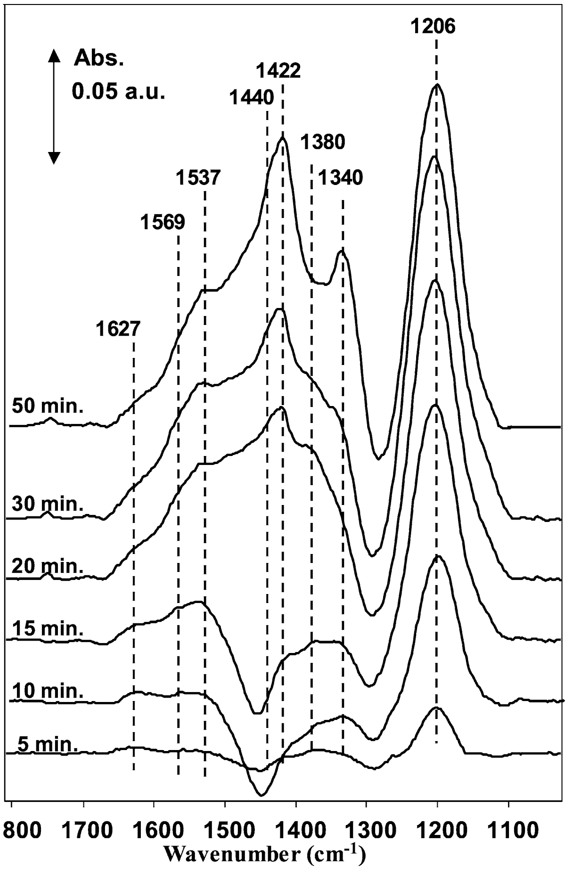


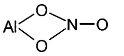
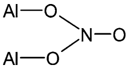
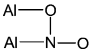
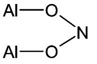
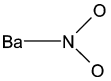
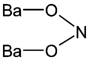
Fig. 2. IR spectra during exposure of the catalyst to 500 ppm NO at 50 °C.

With further NO exposure, bands at 1340, 1380, 1422, 1440, and 1537 cm^{-1} were observed. The broad band at 1537 cm^{-1}, together with the increase of the intensity of the band at 1206 cm^{-1}, is assigned to bridged *N*-coordinated nitrites on Al oxide [6,17]. The assignment of the bands at 1340, 1422, and 1440 cm^{-1} is controversial, because various NO_x species show vibrational modes in the region between 1500 and 1300 cm^{-1}. Prinetto et al. [11] assigned bands at 1375 and 1310 cm^{-1}, detected during NO adsorption, to hyponitrites (NO^-, $N_2O_2{}^{2-}$) formed on sites with high basicity, such as BaO. Monodentate nitrites have bands between 1450 and 1300 cm^{-1} [17,18], whereas linear nitrites affiliated with Ba are reported to exhibit a band around 1420 cm^{-1} [18,19]. All these species could in principle contribute to the broad band observed. Tentatively, these bands are assigned to monodentate nitrites (1340 and 1440 cm^{-1}) and linear nitrites on Ba (1422 cm^{-1}) and hyponitrites (1380 cm^{-1}). The assignments of the various bands to NO_x surface species of adsorbed NO are summarized in Table 1.

3.2.2. *Exposure to NO_2*

The IR spectra during exposure of the catalyst to 500 ppm NO_2 at 50 °C are shown in Fig. 3. At the start of the NO_2 admission, bands at 1203, 1332, and 1419 cm^{-1}, together with a very weak band at around 1621 cm^{-1}, were observed. The bands at 1203 and 1332 cm^{-1} are assigned to bidentate nitrites on BaO. The formation of linear Ba-nitrites, characterized by the weak band at 1419 cm^{-1}, was observed after 5 min of NO_2 adsorption. The weak band at 1621 cm^{-1} is assigned to bidentate nitrates on Al oxide. After 10 min of NO_2 adsorption the band at 1203 cm^{-1} reached its highest intensity and slowly decreased with further exposure. Simultaneously, a new band at 1429 cm^{-1} gradually appeared, while the bands at 1564 and 1479 cm^{-1} increased in intensity with further NO_2 exposure. The band at 1564 cm^{-1} is assigned

Table 1
Assignment of IR bands to surface species formed during adsorption of NO

	NO_x species	Frequency (cm^{-1})	Vibration
Al			
	Chelating bidentate nitrate	1569 1180–1260	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{NO}_{2,\mathrm{as}})$
	Bridging bidentate nitrate	1627 1180–1260	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{NO}_{2,\mathrm{as}})$
Al—O—N—O	Linear nitrite	~ 1480[a], 1537	$\nu(\mathrm{N{=}O})$
	Bridged *N*-coordinated nitrite	~ 1160	$\nu(\mathrm{N{=}O})$
	Bridged bidentate nitrite	~ 1300[a] ~ 1230	$\nu(\mathrm{NO}_{2,\mathrm{as}})$ $\nu(\mathrm{NO}_{2,\mathrm{s}})$
Ba			
Ba—O—N—O	Linear nitrite	ca. 1422	$\nu(\mathrm{N{=}O})$
	Monodentate nitrite	1440 1340	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{N{-}O})$
	Bridged bidentate nitrite	~ 1300[a] ~ 1230	$\nu(\mathrm{NO}_{2,\mathrm{as}})$ $\nu(\mathrm{NO}_{2,\mathrm{s}})$
$\mathrm{N}_2\mathrm{O}_2{}^{2-}$	Hyponitrite	1380/1306	$\nu(\mathrm{N{-}N})$

[a] Possibly masked by bands of decomposing $\mathrm{CO}_3{}^{2-}$.

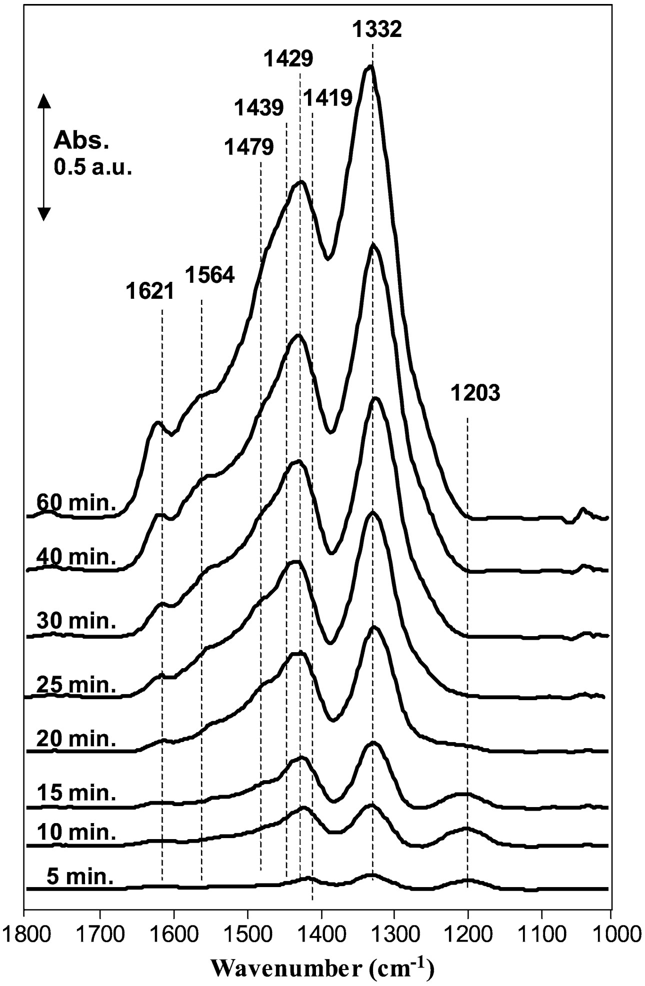
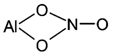
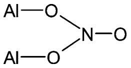
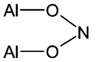
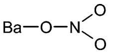
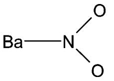
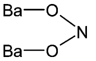


Fig. 3. IR spectra during exposure of the catalyst to 500 ppm NO_2 at 50 °C.

Table 2
Assignment of IR bands to surface species formed during adsorption of NO_2 and NO/O_2

	NO_x species	Frequency (cm^{-1})	Vibration
Al			
	Chelating bidentate nitrate	1564/1561 ~ 1290	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{NO}_{2,\mathrm{as}})$
	Bridging bidentate nitrate	1621/1619 1260	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{NO}_{2,\mathrm{as}})$
Al—O—N—O	Linear nitrite	1479	$\nu(\mathrm{N{=}O})$
	Bridged bidentate nitrite	1200–1230 ~ 1330	$\nu(\mathrm{NO}_{2,\mathrm{s}})$ $\nu(\mathrm{NO}_{2,\mathrm{as}})$
Ba			
	Monodentate nitrate	1429/1424 1332	$\nu(\mathrm{NO}_{2,\mathrm{as}})$ $\nu(\mathrm{NO}_{2,\mathrm{s}})$
Ba—O—N—O	Linear nitrite	1419	$\nu(\mathrm{N{=}O})$
	Monodentate nitrite	1439 1340	$\nu(\mathrm{N{=}O})$ $\nu(\mathrm{N{-}O})$
	Bridged bidentate nitrite	~ 1300 1230–1230	$\nu(\mathrm{NO}_{2,\mathrm{as}})$ $\nu(\mathrm{NO}_{2,\mathrm{s}})$

to chelating bidentate surface nitrates on Al oxide. The corresponding band for the asymmetric vibration, expected between 1200 and 1300 cm^{-1}, was masked by bands of other surface nitrate/nitrite species. The band at 1479 cm^{-1} is assigned to linear nitrites on Al oxide. The bands at 1429 cm^{-1} and the main contribution to the band at 1332 cm^{-1} arise from monodentate nitrates on BaO [13]. Small shoulders, observed at 1439 and 1340 cm^{-1}, could indicate the formation of monodentate nitrites on Ba. The formation of bulk nitrates, with a characteristic band at around 1370 cm^{-1} [6], was not observed. The band assignment for the NO_x surface species during adsorption of NO_2 is summarized in Table 2.

3.2.3. Simultaneous exposure to NO and O_2

The IR spectra during exposure of the catalyst to 500 ppm NO and 5% O_2 at 50 °C are shown in Fig. 4. At the start of the adsorption, a band assigned to surface nitrite species was present at around 1200 cm^{-1}, which reached a maximum in intensity after 18 min adsorption, similar to the situation observed during NO_2 adsorption (Fig. 3). It decreased in intensity with further NO/O_2 exposure. The weak band at 1419 cm^{-1} observed at the beginning of the NO/O_2 adsorption procedure is assigned to linearly bound Ba nitrites. After 10 min of exposure additional bands at 1424 and 1332 cm^{-1} were observed and with further exposure (15 min) overlapping bands at 1619, 1561, 1479, and 1439 cm^{-1} and a weak shoulder at 1260 cm^{-1} were observed.

Bridging bidentate nitrates on Al oxide show a characteristic N=O stretching band at 1619 cm^{-1} and an antisymmetric stretching band around 1260 cm^{-1}(not separated from the other overlapping nitrate bands). Chelating bidentate surface nitrates result in vibrational bands at 1561 and around 1290 cm^{-1} (also overlapping with other ni-

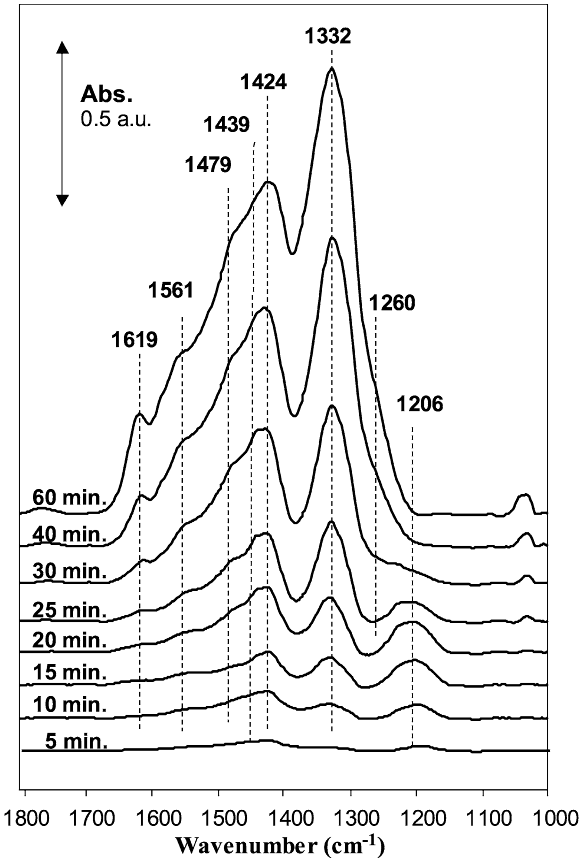


Fig. 4. IR spectra during exposure of the catalyst to 500 ppm NO and 5% O_2 at 50 °C.

trate bands), while linear nitrites on Al exhibit a band at 1479 cm^{-1}. The bands at 1424 and 1332 cm^{-1} are attributed to the presence of monodentate nitrates on Ba oxide sites. The presence of monodentate nitrates on Al could not be unequivocally confirmed because of the unresolved broad bands in the region 1500–1300 cm^{-1}. As also observed for the adsorption of NO_2, the formation of bulk nitrates is negligible, indicated by the absence of the characteristic absorption band for free ionic nitrates around 1370 cm^{-1}. The band assignments for NO/O_2 adsorption are summarized, together with the assignments for NO_2 adsorption, in Table 2.

3.3. Thermal stability of NO_x surface species

The IR spectra during a controlled temperature rise from 50 to 550 °C of the catalysts after exposure to NO, NO_2, and NO/O_2 in an inert gas stream are shown in Fig. 5. For the catalyst preexposed to 500 ppm NO (Fig. 5A), bridged and bidentate nitrates on Al oxide sites with characteristic bands at 1627 and 1574 cm^{-1} and bridged N-coordinated nitrites with characteristic bands at 1536 and 1154 cm^{-1} remained on the surface until 200 °C. The band at 1206 cm^{-1}, attributed mainly to bridged bidentate nitrites, continuously decreased and vanished at around 250 °C. The bands at 1438 and 1342 cm^{-1}(monodentate nitrites) also decreased with increasing temperature. At 200 °C a new band at 1306 cm^{-1} was observed to grow in intensity until 400 °C. During further temperature increase the intensity of this band decreased again, but a small contribution was visible up to 550 °C. This band can be assigned to hyponitrites on Ba oxide, which are reported to be formed during decomposition of NO_x species from highly basic metal oxides preexposed to NO. The high thermal stability observed for these species is in agreement with the literature [20,21]. The negative bands at 1460 and 1370 cm^{-1} result from the further decomposition of residual carbonates during temperature increase.

After preexposure of the catalyst to NO_2 (Fig. 5B), the linear bonded nitrites on Al oxide desorbed at temperatures around 150 °C, shown by a decrease of the band at 1478 cm^{-1}. It was shown that the thermal stability of chelating bidentate nitrates on Al oxide (up to 350 °C) is higher than that to bridged bidentate nitrates on Al oxide (up to 250 °C) [22]. The bands at 1429 and 1332 cm^{-1} can be assigned to monodentate nitrates on Ba, which were thermally stable to temperatures up to 550 °C. At temperatures above 250 °C the band at 1332 cm^{-1} broadened and shifted to lower wavenumbers, indicating an increasing ionic character of the monodentate nitrates. These bands were partly present up to 550 °C.

The thermal stability of the NO_x species formed after exposure of the catalyst to NO and O_2 (Fig. 5C) was similar to that of the species formed upon NO_2 exposure. Among the different nitrite/nitrate species on Ba oxide and Al oxide, the linear and monodentate Ba nitrites had the lowest thermal stability, followed by the bridged and chelating bidentate nitrates on aluminum oxide. At 350 °C, the band assigned to monodentate Ba nitrate (1332 cm^{-1}) shifted to lower wavenumber. The asymmetric stretching vibration of monodentate Ba nitrate around 1425 cm^{-1} was partly masked by the appearance of the negative band at 1450 cm^{-1}, assigned together with a band at 1380 cm^{-1} to the decomposition or replacement of carbonates.

4. Discussion

During the exposure of the catalyst to NO, predominantly nitrite surface species are formed on Ba oxide and Al oxide sites. Initially, linear and bridged nitrites are formed, which were preferably located on Ba oxide surface sites, due to their higher basicity [23]. It is likely that the nitrite first interacts via the positively charged N atom with the negatively charged oxygen atom next to Ba creating a linear nitrite species [24] as shown in Scheme 1.

If linear Ba nitrites are formed on less coordinated surface oxygen sites they could subsequently interact via the oxygen of NO with an adjacent Ba atom and lead to the formation of bridged Ba nitrites, as shown in Scheme 2.

Simultaneously with the formation of nitrites, the amount of Ba carbonate species decreased, which indicates the partial replacement of carbonates by the nitrites formed on

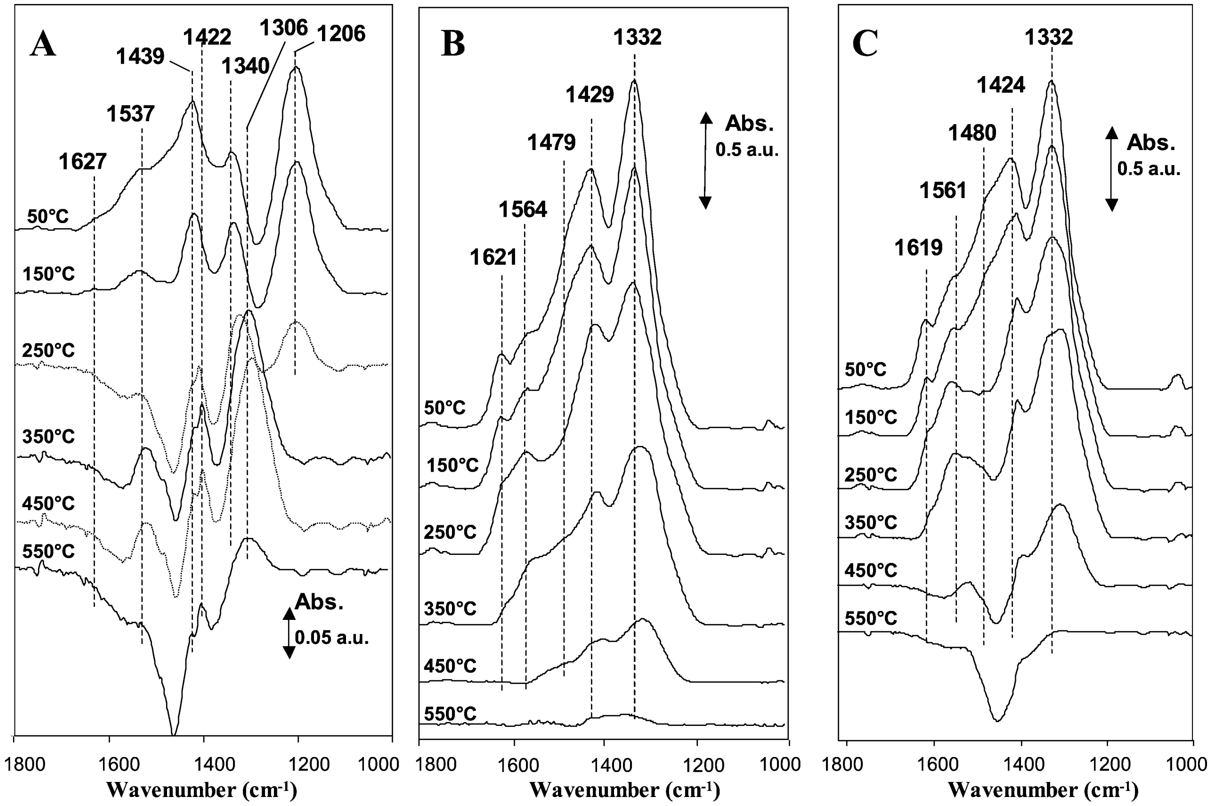
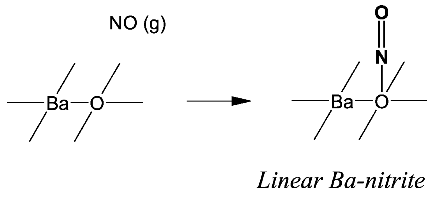


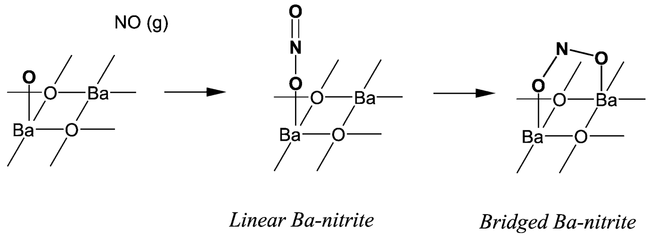
Fig. 5. IR spectra during temperature increase from 50 to 550 °C of the pre-exposed catalyst in an inert gas stream: (A) after exposure of the catalyst to 500 ppm NO at 50 °C; (B) after exposure to 500 ppm NO_2 at 50 °C; and (C) after exposure to 500 ppm NO and 5% O_2 at 50 °C.

BaO. The decomposition of surface carbonates, however, was only detected during the exposure of the catalyst to NO and NO/O_2, but not during the exposure of the catalyst to NO_2. Therefore, NO appears to be the active species during the replacement of barium carbonates on the surface of the catalyst. On metal oxide surfaces carbonates exist in monodentate, chelating, and bridged forms [25,26]. The reaction steps for the replacement of monodentate and bidentate carbonates by forming linear and bridged nitrites could be proposed according to Scheme 3 and 4. With further exposure of the catalysts to NO, Al oxide sites are also concluded to be involved in the storage process. The main species being formed are linear N-coordinated nitrites. It is interesting to note that bands characteristic of bridged and chelating nitrates on Al sites were observed in the absence of gas phase O_2.

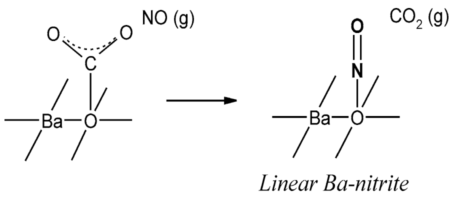
For nitrate formation from NO different pathways are plausible. One possibility is the presence of reactive oxygen species on the catalyst surface, such as peroxides or defect metal sites on the surface of Ba oxide or Al oxide. As the formation of peroxides on Al oxide is negligible, even when O_2 is present in the feed [6], Ba peroxides are the only plausible source for highly reactive oxygen. However, because of the higher basicity of BaO, the spillover of the NO_x species to Al oxide sites after oxidation does not seem to be likely. Therefore, linear N-coordinated nitrites and linear nitrites on Al oxide sites are expected to act as intermediates during the nitrate formation via coordinatively unsaturated metal cations. Bands for linear nitrites could not be clearly identified, due to the negative band in this region arising from the carbonates replaced; however, N-coordinated nitrites were observed. Thus, the bridging and chelating bidentate Al-nitrates are speculated to be formed on cation vacancy sites on the alumina surface.



Scheme 1.



Scheme 2.



Scheme 3.

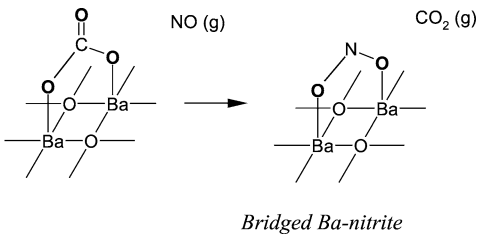
Summarizing these observations, four parallel reaction steps for the adsorption of NO were identified:

(i) Molecular adsorption of NO by formation of nitrites on BaO sites;
(ii) (Partial) replacement of Ba carbonates by NO, resulting in the formation of Ba nitrites;
(iii) Formation of hyponitrites on BaO sites;
(iv) Formation of bridging and chelating bidentate nitrates on Al oxide via the formation on cation vacancy sites on the Al oxide surface.

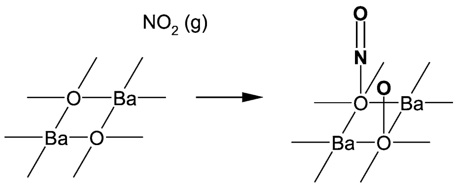
It should be noted, however, that the amount of adsorbed NO_x species during the exposure of the catalyst to NO is much lower than in the exposure to NO/O_2 and NO_2.

The main surface species formed during exposure of the catalyst to 500 ppm NO_2 are nitrates formed on alumina and barium oxide sites. Surface nitrites seem to play, however, an important role as an initial step in the storage process. Similarly to the exposure of the catalyst to NO, bridged and linear nitrites on Ba oxide and Al oxide were observed at the beginning of the NO_2 exposure. Bridged nitrites could be generated via molecular adsorption of NO_2 on two neighboring BaO sites, whereas for the formation of linear nitrites the presence of NO is necessary. Broqvist et al. [27] investigated NO_2 adsorption at a BaO (100) surface by density functional theory calculations and proposed a mechanism in which nitrites are generated during pairwise NO_2 chemisorption on Ba and O sites with a subsequent redox reaction of both with adsorbed NO_2 species forming a nitrite–nitrate pair. Schneider et al. [28] proposed a similar adsorption–oxidation mechanism for two NO_2 molecules for the formation of nitrates on MgO. Dissociative adsorption of NO_2 was proposed by Schmitz, Baird [24], who investigated NO_2 adsorption at BaO films with XPS. They postulated adsorption of NO_2 onto the BaO surface via a dissociation of the NO_2, creating linear Ba nitrites and BaO_2. As in our experiments only insignificant amounts of Ba nitrates were detected during the initial formation of linear Ba nitrites, a dissociative adsorption of NO_2 (Scheme 5) seems to be more likely.

The decreasing concentration of bridged nitrites with increasing time of exposure could result from an oxidation of Ba nitrites with gas-phase NO_2 creating bridged bidentate nitrates or by direct replacement of nitrites by nitrates formed on adjacent sites and subsequent surface transport. Monodentate nitrites and nitrates on Ba are formed by the molecular adsorption of NO_2 at a Ba and an O site, respectively [21].



Scheme 4.



Scheme 5.

The reaction steps derived from the sorption of NO_2 on the NSR catalyst could be summarized as follows:

(i) Bridged nitrites form via adsorption of NO_2 on two adjacent metal sites;
(ii) Linear nitrites form via a dissociative adsorption of NO_2;
(iii) Nitrites are oxidized by gas phase NO_2 or directly replaced by nitrates after extended exposure;
(iv) Nitrates are the main species after extended NO_2 exposure.

As mentioned above, the decomposition or replacement of the remaining Ba carbonates, indicated by negative bands in the difference IR spectra, did not occur during exposure of the catalysts to NO_2. The replacement of carbonates was only observed when NO was present in the feed. In this context, it should be mentioned that Balcon et al. [29] and Amberntsson et al. [30] investigated the influence of CO_2 on the release of NO_x stored on a barium-containing NSR catalyst at temperatures between 250 and 550 °C and observed a promoting effect of CO_2 on the release of NO_x. Balcon et al. [29] suggested competitive storage of CO_2 and NO_2 for the same barium site and interpreted this in terms of the existence of the equilibrium $CO_{2(g)}$ + Ba nitrates $\rightleftarrows$ $NO_{2(g)}$ + Ba carbonates, which would explain the inactivity of NO_2 for Ba carbonate replacement observed during the exposure of the catalyst to NO_2. However, based on our observation that a replacement of carbonates was observed during exposure to NO or NO/O_2, it could be speculated that a comparable equilibrium for NO $\leftrightarrow$ CO_2 storage on Ba sites does not exist, or that under the reaction conditions used, the equilibrium is shifted toward the formation of Ba nitrites and the release of CO_2.

Exposure of the catalysts to NO and O_2 led to results similar to those from the exposure to NO_2. The main differences observed are that bridged nitrites were observed for a longer period and that nitrate species are formed at lower concentrations (around 80% of the amount of nitrates formed during exposure to NO_2), while the concentration of nitrite species formed was equal to the concentration formed during NO_2 exposure. Compared to the NO exposure, the amount of Al nitrates is much higher and additional Ba nitrates are present on the catalyst surface after NO/O_2 exposure.

As NO_2 formation via NO oxidation on Pt is known to occur at temperatures above 150 °C, this reaction can be neglected as the main source for NO_2 formation [6]. Therefore, the similarity of the surface species observed during exposure to NO_2 and NO/O_2 is unexpected. As the thermodynamic equilibrium for the reversible gas phase reaction of NO with O_2 forming NO_2 at low temperatures is on the side of NO_2 [31], a minor contribution of NO_2 forming surface nitrates could arise from the gas-phase reaction of NO with O_2. Additionally, a small amount of nitrates is speculated to be formed via defect sites on Al oxides and Ba oxides, as already postulated for the Al nitrates formed during exposure to NO. A third pathway for nitrate formation could be related to reactive oxygen species present on the metal surface. Several research groups investigated the interaction of O_2 with metal oxide surfaces (e.g., BaO, MgO, La_2O_3, Tb_4O_7) and proposed a molecular and a dissociative adsorption mechanism for O_2 [22,32]. Thus, the formation of nitrates on Ba oxide and Al oxide could occur via the reaction of nucleophilic oxygen adsorbed on the surface with a NO molecule. A molecular and dissociative adsorption of O_2 on BaO and Al_2O_3 is also confirmed by results reported by Sedlmair et al. [33] for the adsorption of NO and O_2 on Ba-exchanged Y zeolites containing no Pt. They observed similar amounts of surface nitrates formed during the exposure to NO/O_2 and NO_2 at 50 °C and explained this by a molecular and dissociative adsorption of O_2 on the metal surface sites forming reactive oxygen surface species. As small amounts of La oxides and Ce oxides are present in the NSR catalysts these species could also be assumed to act as sources for reactive oxygen species. Among all three possible pathways for nitrate formation the last one, which involves reactive oxygen species, is speculated to be the most important.

The longer presence of bridged nitrites during NO/O_2 exposure compared to NO_2 exposure indicates the slow oxidation of NO to nitrates. This observation and the lower concentration of nitrates formed during NO/O_2 adsorption suggest that oxidation with NO_2 as oxidation agent is more important than oxidation with gas-phase oxygen.

The thermal stability of the NO_x species formed on the catalyst upon exposure to NO, NO_2 and to NO/O_2 is comparable. In all cases nitrates show higher thermal stability than nitrites. In general, nitrites and nitrates formed on Ba oxide were more stable than those formed on Al oxide. Hyponitrites, only detected after the exposure of the catalyst to NO, show a high thermal stability, in contrast. The shift of the monodentate Ba nitrate bands to lower wavenumbers during temperature increase indicates a change in the covalent–ionic bonding character of the nitrates. For covalently bound nitrates an IR band around 1470 cm^{-1} is expected, whereas for ionically bound nitrates an IR band is located at around 1370 cm^{-1} [34]. Therefore we conclude that the ionic bonding character of Ba nitrates increases with increasing temperature. The presence of ionic bulk-like nitrates after heating to 550 °C suggests a partial migration of surface Ba nitrates into the bulk.

5. Conclusions

Surface species and reaction intermediates on a commercial NO_x storage–reduction catalyst during exposure to NO, NO_2, and NO/O_2 have been identified by in situ IR spectroscopy. During exposure of the catalyst to NO, mainly linear and bridged nitrites were formed by molecular adsorption of NO. After longer exposure, small concentrations of bridged and chelating nitrates on Al oxide sites were seen, which were formed via the oxidation of NO by reactive oxygen and via oxidation of adsorbed nitrites.

The main surface species formed during the exposure of the catalyst to NO_2 and NO/O_2 are nitrates on the Al oxide and Ba oxide catalyst components. A higher concentration of adsorbed nitrate species was found for NO_2 exposure than for NO/O_2 exposure. Nitrites were identified as intermediates during the formation of nitrates. For the formation of linear nitrites a dissociative adsorption mechanism of NO_2 on Ba oxide sites is proposed. After longer exposure, nitrites are either oxidized by NO_2 to nitrates or directly replaced by nitrates. In particular, chelating, bridging, and monodentate nitrates are the main NO_x species formed on the Ba oxide and Al oxide sites during exposure to NO/O_2 or NO_2. The total amount of NO_x species adsorbed is the lowest for NO exposure, followed by NO/O_2 and NO_2 exposure. NO was found to be the active species for replacement of Ba carbonates by Ba NO_x species.

The thermal stability of the NO_x species formed on the catalyst increases in the order Al nitrites (linear, N-coordinated) $<$ Ba nitrites (linear, monodentate) $<$ Al nitrates (bridging bidentate, chelating bidentate) $<$ Ba hyponitrites $<$ Ba nitrates (monodentate).

The results clearly indicate the presence of a series of subsequent reaction steps during the adsorption of NO_x on a NSR catalyst. The proposed key elementary steps are summarized in a general scheme shown in Fig. 6. Initially NO is stored in the form of nitrites on the storage component either by molecular adsorption on Al oxides and Ba oxides (a) or by the replacement of Ba carbonates (b). NO_2 formed by oxidation on the noble metal either sorbs molecularly and forms nitrates (c) or sorbs dissociatively and forms nitrites (d). After a certain concentration of NO_x is adsorbed, the transformation and further oxidation of the surface nitrites into surface nitrates by NO_2 (e) is the predominant reaction step during the storage of NO_x on the catalysts.

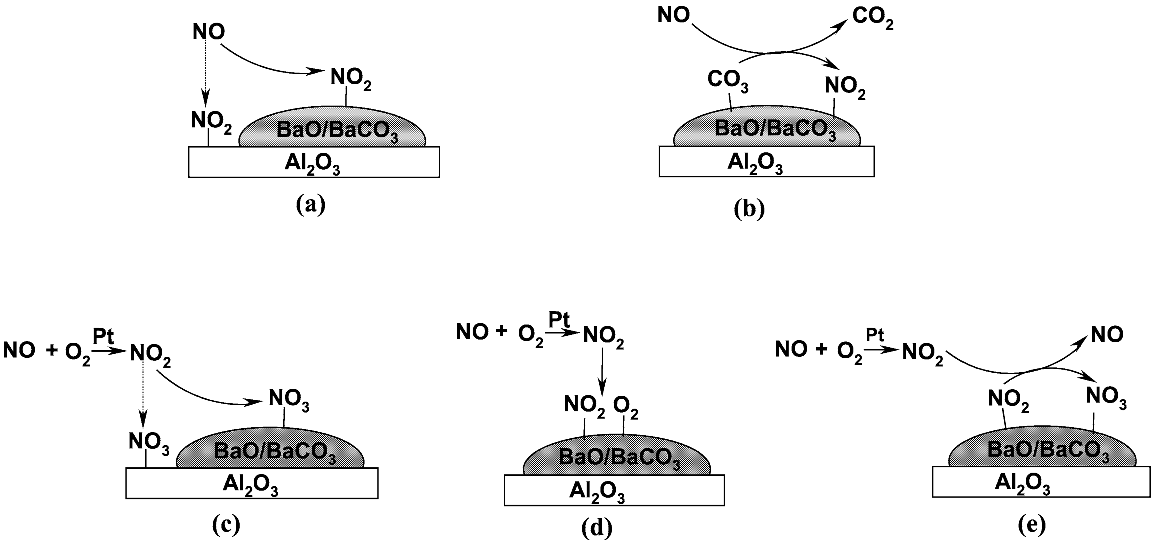


Fig. 6. General molecular scheme of the main elementary steps for NO_x storage on a commercial storage reduction catalyst. (a) Formation of nitrites by molecular adsorption of NO; (b) replacement of Ba carbonates with Ba nitrites formed by NO; (c) formation of nitrates by molecular adsorption of NO_2; (d) formation of Ba nitrites and Ba peroxides by dissociative adsorption of NO_2; (e) transformation of surface nitrites to surface nitrates with NO_2 as oxidizing agent. Note that in all schematic structures of surface species shown one oxygen arises from the Al oxide or Ba oxide surface.

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