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CeO_2 catalysed soot oxidation
The role of active oxygen to accelerate the oxidation conversion

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Abstract

The influence of CeO_2 in the acceleration of NO_x-assisted soot oxidation has been studied in flow-reactor equipment by comparing two catalyst configurations, namely: (1) Pt upstream of soot and (2) Pt upstream of CeO_2-soot. The role of CeO_2 has been elucidated by means of DRIFT spectroscopy coupled with mass spectrometry and TAP reactor experiments. It was found that CeO_2 has the potential to accelerate the oxidation rate of soot due to its active oxygen storage. The formation of active oxygen is initiated by NO_2 in the gas phase. A synergetic effect is observed as a result of surface nitrate decomposition, which results in gas phase NO_2 and desorption of active oxygen. Stored oxygen is postulated to exist in the form of surface peroxide or super oxide. Active oxygen is likely to play a role on the acceleration of soot oxidation and to contribute more than desorbed NO_2 or NO_2 from surface nitrate decomposition.

Keywords: Soot oxidation; NO_2; CeO_2; Active oxygen

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1. Introduction

Due to the environmental and health effects of diesel soot and the pressure to comply with the emissions regulations, it is not surprising that reduction of diesel soot emission has gained a lot of attention. Efforts to reduce the emissions are ongoing and remain a challenging topic. One of the reduction strategies is to employ a diesel after-treatment system onto the exhaust. Soot-trapping followed by oxidation with the highly reactive NO_2 is an example and the basis of the so-called Continuously Regenerating Trap (CRT) [1] and the TU Delft filter [2]. These filter systems contain a platinum catalyst upstream of a soot trap. The main differences are as follows. In the CRT system Pt is loaded on a flow-through monolith, while in the TU Delft filter Pt catalyst is loaded on ceramic foam. In the CRT system the Pt coated flow-through monolith functions only as NO_2 generator, no soot trapping or soot oxidation is aimed for. In the TU Delft filter a Pt/ceramic foam catalyst is designed as a multifunctional reactor that functions not only as NO_2 generator but also as soot filter; a specific advantage is that NO_2 is used catalytically, viz. every NO_2 is used more than once. In both systems NO_2 is generated that passes through the wall-flow monolith where it reacts with the trapped soot.

So far, both in the laboratory and real life application, the oxidation of soot with NO_2 has been explored only as a non-catalytic reaction, for example in [3]. Combination with a catalytic system that accelerates the reaction could be a major improvement. Catalysis by a metal oxide might be an option. Among metal oxides CeO_2 has been proven to have potential in the oxidation of soot [4]. For example, cerium compound has been used as fuel additive. The first effect of the cerium fuel additive is to reduce the amount of engine-out particulate [5]. The second effect of the cerium additive is that it enhances the reactivity of the soot formed. Upon deposition on the filter, CeO_2 is present in the soot particulate a very fine particle size of about 5–25 nm [6]. In this way CeO_2 acts as an oxidation catalyst (fuel borne catalyst) in the regeneration of trapped particulate matter [7,8]. In combination with traces of platinum catalyst, cerium present in the activated soot showed synergetic effect in the oxidation of soot with NO and O_2 [9]. Although ceria has been used as fuel borne catalyst, the catalysis of soot oxidation by CeO_2 in the presence of NO and O_2 remains unclear.

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The acceleration of the NO_2-soot reaction by CeO_2 is postulated to occur according to the following processes:

(a) CeO_2 might catalyse the oxidation of NO to NO_2, as a result additional NO_2 is available for the NO_2-soot reaction
(b) At low temperature, CeO_2 adsorbs NO_2 in the form of cerium nitrate. At high temperature cerium nitrate is decomposed and NO_2 is produced. This NO_2 again contributes to accelerate the soot-NO_2 reaction.
(c) NO_2 interacts with CeO_2 to create cerium peroxide or super-oxide. The peroxide or super-oxide is decomposed at higher temperatures and contributes to increased oxidation rate.

The interaction of NO_2 with CeO_2 has been demonstrated by means of X-ray absorption near-edge spectroscopy (XANES) [10,11]. The interaction was described by the following reactions:

(a) direct interaction of NO_2 with the O centre of the oxide:

$$NO_2(\text{gas}) + O(\text{lattice}) \Rightarrow NO_3(\text{adsorbed}) \quad (1)$$

(b) reactions that involve metal centres that may contain oxygen vacancies:

$$NO_2(\text{gas}) + Ce \Rightarrow Ce - O + NO(\text{gas}) \quad (2)$$

$$NO_2(\text{gas}) + Ce - O \Rightarrow CeNO_3(\text{adsorbed}) \quad (3)$$

This NO_3 species is concluded to be stable up to 450 and 600 K. This type of interaction is observed in several metal oxides: MgO, TiO_2, Fe_2O_3, CuO and ZnO [11].

In the present study, the potential of CeO_2 in the acceleration of the NO_2-soot-based reaction is examined. The first objective is to explore the catalytic effect of CeO_2 on the NO_2-assisted soot oxidation rate under continuous conditions. The second is to investigate the surface interaction of NO_2 with CeO_2. The decomposition products of the surface species are thought to be responsible for the increase of the soot oxidation rate. To elucidate the synergetic oxidation mechanism DRIFT analysis coupled with mass spectrometry and an advanced Temporal Analysis Products (TAP) reactor system was used.

2. Experimental

2.1. Materials

A Pt/alumina catalyst was prepared by incipient wetness impregnation. Eight grams of 63–100 μm γ-alumina (AKZO-Nobel 003–1.5e) was impregnated by 10 ml 15 g/l $[Pt(NH_3)_4]Cl_2$ solution, dried for 2 h at 355 K and calcined at 725 K for 2 h. The model soot used is Printex-U. This model soot was proven to be an appropriate model for the NO_2-soot-based reaction [12]. CeO_2 was made by calcination of $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich) at 723 K in furnace with a continuous flowing air stream for two hours. The particle size was 63–100 μm (determined from powder XRD pattern). The pattern shows that the sample contains only CeO_2 phase. The BET specific surface area of the sample measured by Quantachrome Autosorb-6B is 85 (±1) m^2/g, which is in agreement form the calculation of CeO_2 particle size distribution as obtained from XRD measurements.

2.2. Flow reactor experiments

The flow-reactor equipment described in [12] was used to examine the influence of CeO_2 in NO_2-assisted soot oxidation. A quartz reactor with 6 mm inner diameter was filled with two separate beds, a soot bed placed downstream of a Pt/alumina bed. Quartz wool was used to separate the two beds. The soot bed contains 20 mg soot physically mixed with 40 mg CeO_2 and 400 mg SiC in a so-called a ‘loose contact’ procedure, while the Pt/alumina bed contains 40 mg 1% Pt/alumina mixed with 400 mg SiC. In another reactor 20 mg soot was mixed with 400 mg SiC and placed downstream of the Pt catalyst bed. Several reference experiments were also done for comparison. The samples were heated to 900 K at a heating rate of 0.6 K/min. Unless otherwise stated, the gas composition used is 700 ppm NO + 10% O_2 with argon as balance gas. A NDIR and a NO_x analyser are placed downstream of the reactor to analyse the reaction product. The carbon mass balance is closed between 95 and 110%. Previous research had shown at under the applied reaction conditions the reaction will run under kinetic controlled conditions [2].

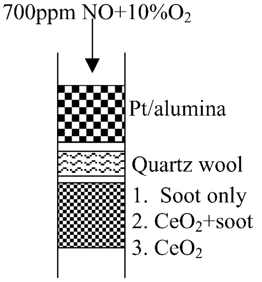
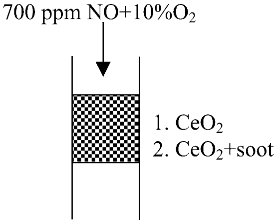
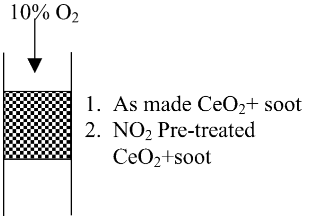
To check if pre-treatment by NO_2 and O_2 can influence the activity of CeO_2 in the oxidation of soot with O_2, CeO_2 was pre-treated by flowing 300 ppm NO_2 and 10% O_2 in the flow reactor for 4 h Subsequently, 20 mg soot was added into the reactor and gently mixed with the pre-treated CeO_2. The activity of the pre-treated sample was then tested in the oxidation of soot with 10% O_2 in Ar with the same procedure as explained before. Experiments in the flow reactor are summarised in Table 1.

2.3. DRIFT analysis coupled with mass spectrometry

A Nicolet Magna 850 spectrometer using a Spectratech diffuse reflectance accessory equipped with a high temperature cell was used. The equipment and the reactor cell are described in [13]. The amount of CeO_2 used was about 20 mg. Prior to the NO_2 exposure the sample was heated in flowing He, 30 ml/min flow rate, to 723 K and kept there for 30 min to remove possible adsorbed species. The sample was then cooled down to 673 K where background spectra were taken. The background spectra were also taken at 623, 573, 523 and 473 K, respectively. All spectra were recorded at 64 scans with 4 cm^{-1} resolution.

A 20 ml/min gas containing 1100 ppm NO_2 in He were flown over the sample at 473 K. The spectra of adsorbed species were measured at this temperature until spectral

Table 1
Reactor bed configurations for catalyst activity of soot oxidation and NO oxidation to NO_2

Bed configurations	Aspects to observe
	1. NO_x assisted soot oxidation rate without CeO_2 2. NO_x assisted soot oxidation rate with CeO_2 3. Effect of CeO_2 down stream Pt catalyst on the formation of NO_2
	1. Catalytic activity of CeO_2 in the formation of NO_2 without Pt catalyst 2. Oxidation rate of CeO_2-soot
	Effect of NO_2 pre-treated CeO_2 on the oxidation rate of soot with O_2

changes were no longer observed. After exposure to NO_2 for about 60 min, the gas flow was switched to He. Two minutes later, a temperature programme of 15 K/min was applied to remove the adsorbate. During heating in He the spectra were measured at 523, 573, 623, 673 and 723 K. Simultaneously, the gas emissions were recorded by a mass spectrometer (Thermostar^{TM} from Pfeiffer Vacuum). The emissions of mass 30, 32, 44 and 46 attributed to NO, O_2, N_2O and NO_2, respectively, were examined. Similar procedures were done with about 1100 ppm $NO_2 + 10\%$ O_2 and only 10% O_2.

2.4. TAP reactor experiment

An advanced Temporal Analysis Products (TAP) reactor system was used to study the interaction of O_2 with CeO_2 and Al_2O_3 as a function of temperature. In the TAP reactor system, a fixed bed reactor is located in an ultra high vacuum system. Small amounts of reactants (10^{15}–10^{20} molecules) can be pulsed into the reactor. At the reactor exit the pulse response is simultaneously analysed by four quadrupole mass spectrometers. A detailed description of the TAP reactor set-up has been previously reported [14].

3. Results

3.1. Effect of CeO_2 on NO_x-assisted soot oxidation rate

In Fig. 1, $CO + CO_2$ emissions as a function of temperature for various catalyst-soot configurations, namely: (1) CeO_2-soot, (2) Pt upstream of CeO_2-soot and (3) Pt upstream of soot, using $NO + O_2$ in the gas stream are displayed. Since the amounts of soot loaded are approximately the same and the same constant heating rate were used, these $CO + CO_2$ emissions reflect relative oxidation rate of the systems. The oxidation profile of non-catalytic soot oxidation with $NO + O_2$ is incorporated for comparison. A similar profile is observed when Al_2O_3 is mixed with soot in the reactor bed. When the feed gas consists of O_2, without NO, the CeO_2-soot and Pt-soot systems resemble the non-catalysed case.

When CeO_2 was physically mixed with soot (configuration 1), the oxidation profile in $NO + O_2$ has shifted to lower temperatures compared to that of non-catalytic soot oxidation. When a Pt catalyst was placed upstream of CeO_2-soot mixture (configuration 2), a significant additional shift is observed. Without CeO_2 in the soot bed downstream of Pt catalyst, i.e. configuration 3, the oxidation profile consists

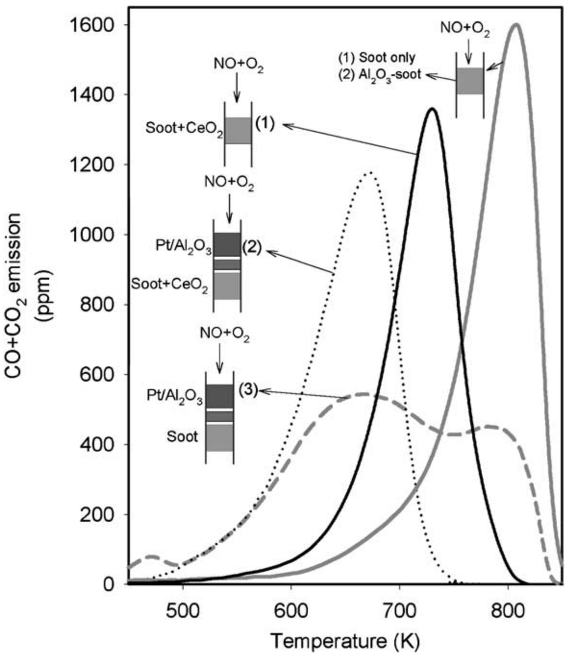


Fig. 1. Demonstration of CeO_2 catalysed NO_x-assisted soot oxidation in Pt upstream of CeO_2-soot and CeO_2-soot configurations, temperature programmed oxidation and heating rate of 0.6 K/min.

of a double peak, one coinciding with that of configuration 2 and one coinciding with the non-catalysed reaction.

To evaluate if the presence of CeO_2 in configuration 2 could increase the amount of NO_2, the rate of NO_2 formation in NO/O_2 feed was measured for the different components in the configurations studied. The results are shown in Fig. 2.

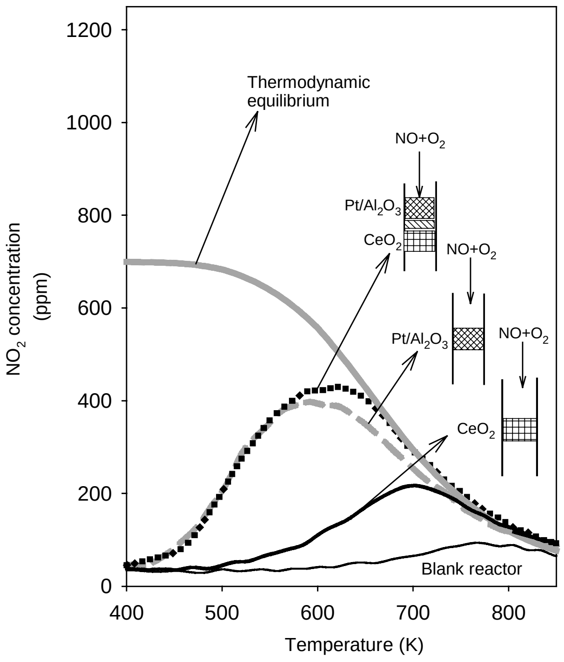


Fig. 2. The influence of CeO_2 in the formation of NO_2 in Pt upstream of CeO_2 bed, temperature programmed oxidation and heating rate of 0.6 K/min.

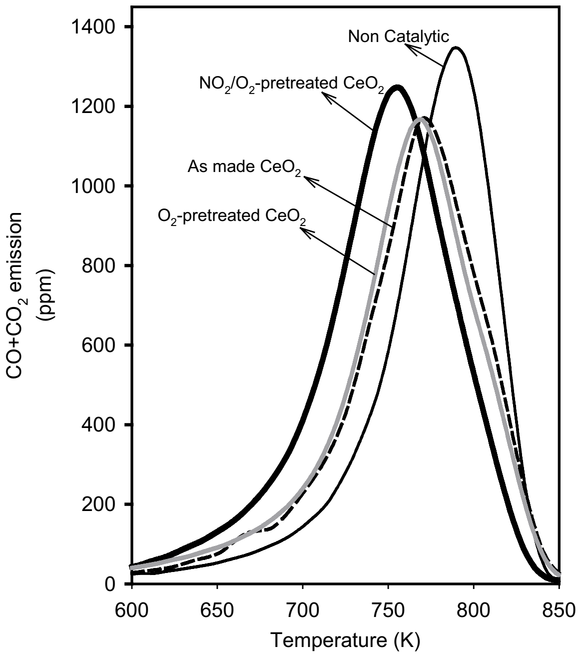


Fig. 3. The influence of NO_2 and O_2 pre-treated on the CeO_2 catalysed soot oxidation with O_2, temperature programmed oxidation and heating rate of 0.6 K/min.

All systems exhibit catalytic activity but platinum is much more active than CeO_2.

To check for the occurrence of CeO_2 activation by NO_2 or O_2 storage, the catalysts were pre-treated by exposing them to 300 ppm NO_2 + 10% O_2 and 10% O_2 at 473 K. Subsequently, the activity in the oxidation of soot with O_2 was tested. The results are shown in Fig. 3. It can be seen that pre-treatment by O_2, does not influence the activity of CeO_2, while 300 ppm NO_2 + 10% O_2 significantly increases the activity.

3.2. Interaction of NO_2 with CeO_2; mass spectrometry and DRIFT spectroscopy data analysis

Fig. 4 represents the mass spectrometry data of mass 30, 32, 44 and 46 attributed to NO, O_2, N_2O and NO_2, respectively, detected during the exposure of CeO_2 to 1100 ppm NO_2 followed by heating in He. After the gas flow was switched from He to He + NO_2 at 473 K, besides NO_2, NO and N_2O emissions are also observed, but no O_2 emission is detected. As the exposure continues the NO signal increases sharply for about 15 min, reaches a maximum and then decreases. N_2O sharply increases after switching followed by a constant signal. The signal of NO_2 also rises sharply after switching for the first 3 min and followed by a rather slow increase.

After being exposed to NO_2 for about 60 min, the gas flow was switched to He. Two minutes later, when a temperature programme of 15 K/min was applied, immediately NO_2 emission is observed, already at 550 K. The emission of NO and O_2 during this heating program is observed only

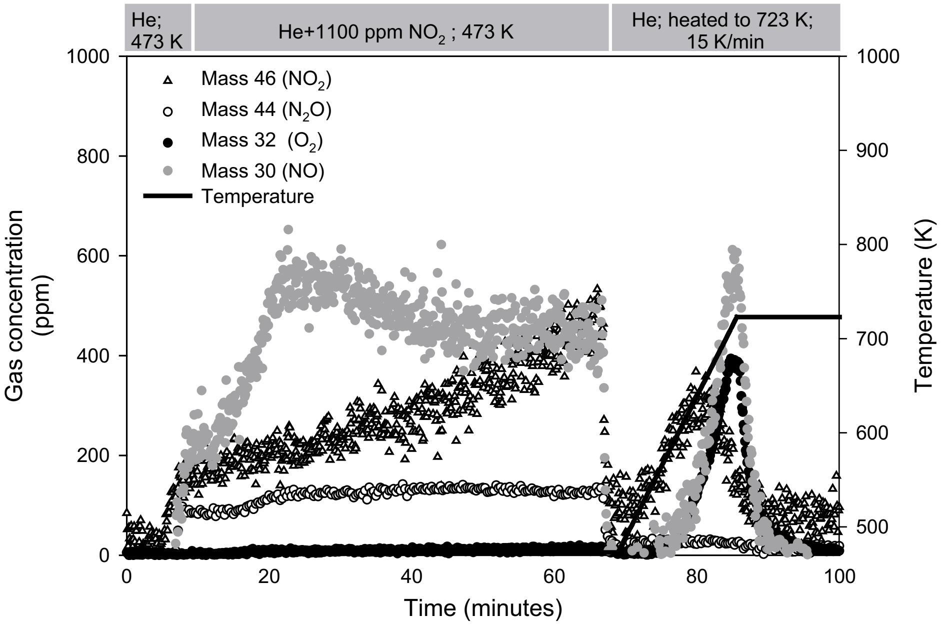


Fig. 4. Mass spectrometry of NO, O_2 and NO_2 emission during the exposure to 1100 ppm NO_2 and the heating in He with temperature programmed of 15 K/min.

above 600 K with about the same initial amounts. During this temperature programme, no significant N_2O emission is observed. When the sample was exposed to 10% O_2 with the same procedure neither O_2 nor nitrogen oxide emission was observed following heating (not shown).

Simple calculation was done to estimate the amount of NO_2 and O_2 adsorbed on CeO_2. The total amount of NO_x (the sum of NO, N_2O and NO_2) emitted during exposure is less than 1100 ppm, the undetected amount is referred to as adsorbed NO_2. The emission of NO and N_2O during the exposure period is believed to be due to NO_2 that has transferred its oxygen atom to CeO_2. Therefore, the total amount of NO and N_2O emitted should be equivalent with the amount of oxygen atoms adsorbed. These mass balance calculation results are shown in Table 2. The amount of desorbed NO_2 is calculated from the total amounts of NO_2, N_2O and NO in the desorption step. About 90% NO_2 is recovered. The amount of O_2 produced from nitrate decomposition is proportional with NO and N_2O observed during the heating programme. This means that 2.2 μmol O_2 was produced from nitrate decomposition. It can be calculated that only about 10% of adsorbed O_2 is recovered in the desorption step.

Table 2
NO_2 and O_2 mass balance during exposure to NO_2 followed by TPD in He

NO_2 (μmol)		O_2 (μmol)	
Uptake[a]	Recovered	Uptake[b]	Recovered
11.8	NO_2:5.5 NO:3.6 N_2O:0.7	12.1	3.3

[a] Calculated from undetected NO_x.

[b] Calculated from NO and N_2O emissions during exposure to NO_2.

The surface coverage of CeO_2 was calculated based upon the total amount of adsorbed NO_2 and O_2. The cross sectional molecular area for O_2 and NO_2 were taken from [15,16], which are 14.1 and 15.1 A^2, respectively. The area covered by O_2 and NO_2 is found to be 2.09 m^2 while the total surface area of the applied amount CeO_2 is 1.70 m^2.

To correlate the dynamics of surface species with the gas phase observations, DRIFT spectra of the NO_2–CeO_2 surface interaction were examined. Prior to the NO_2 exposure the spectra of the sample in flowing He were recorded at 473, 523, 573, 623, 673 and 723 K as reference and used as background spectra. The DRIFT spectra of CeO_2 measured during the exposure to 1100 ppm NO_2 at 473 K covering the wave number of 850–1800 cm^{-1} are presented in Fig. 5a. After 1 min exposure to NO_2, several peaks are immediately observed. Although IR assignments of NO_x^- species are usually related to measurements at ambient temperature, as in [17,18] and there is large disagreement among them, the spectral interpretation summarised in [18] is used as a reference to identify the surface species in the present system. The assignments for the spectra up to 10 min exposure are related to chelating nitro compounds (ca. 1500 and 1157 cm^{-1}), monodentate nitrite (ca. 1460 and 1097 cm^{-1}) and a nitro compound (ca. 1300 and 1405 cm^{-1}). Starting from 20 min, some new peaks are observed up to 60 min where stable spectra were obtained. The assignments for these spectra are bridging nitrate (ca. 1596, 1208 and 995 cm^{-1}), bidentate nitrate (ca. 1574, 1270 and 1026 cm^{-1}) and monodentate nitrate (ca. 1545, 1237 and 995 cm^{-1}). The 1360 cm^{-1} peak

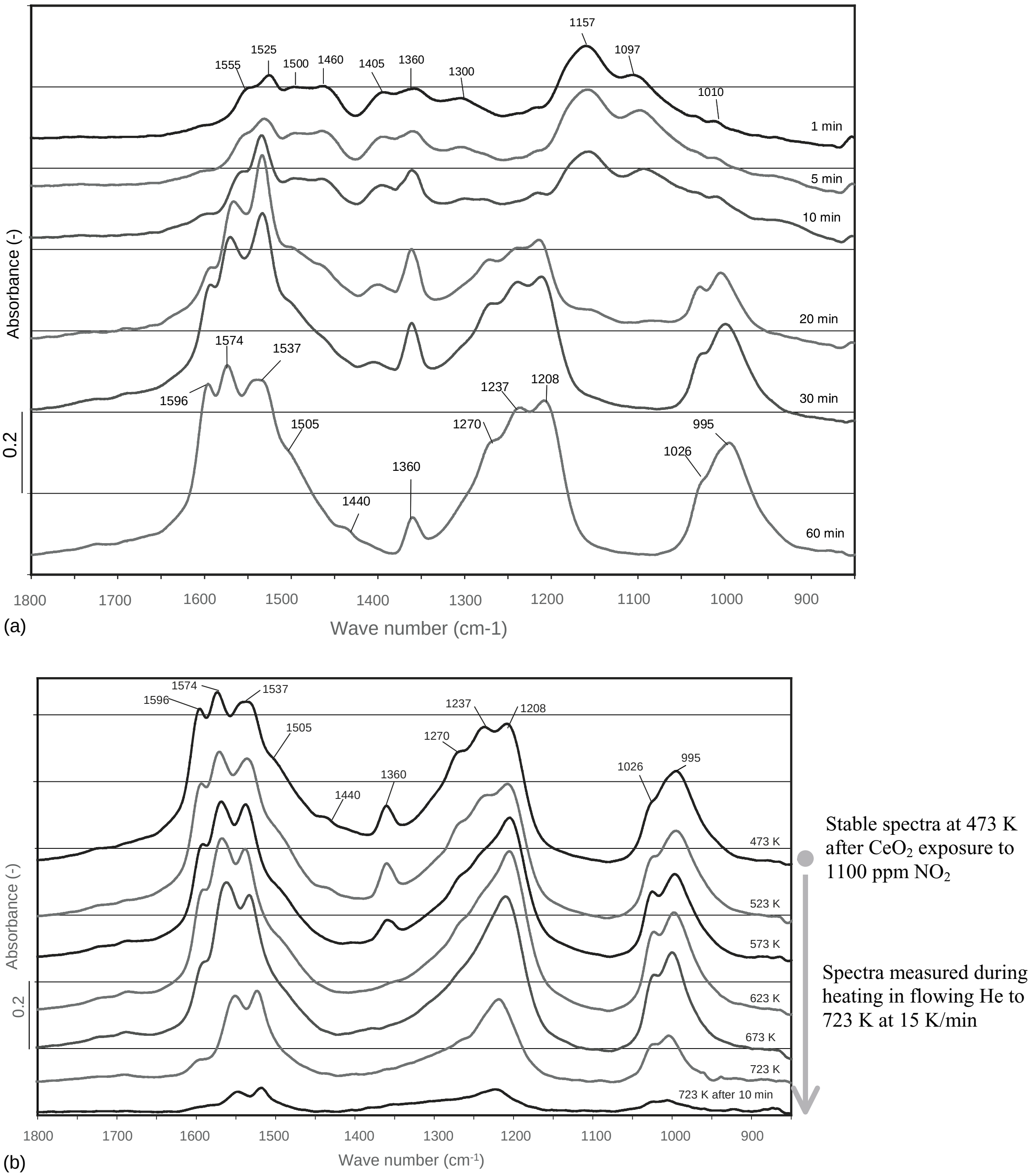


Fig. 5. (a) DRIFT spectra of CeO_2 during exposure to 1100 ppm NO_2 at 473 K. (b) DRIFT spectra of CeO_2 after exposure to 1100 ppm NO_2 at 473 K followed by heating at 15 K/min.

is assigned as the CeO_2 surface nitrite–nitrato. In [19] wave number of 1360 is usually assigned as nitrite–nitrato formed on the high temperature-cell window. In the stable spectra the chelating nitro compounds are observed as ca. 1237 and 1505 cm^{-1} while the 1440 cm^{-1} probably originated from the nitro compound.

After the stable spectra were obtained the sample was heated from 473 to 723 K in He at 15 K/min. The spectra were recorded at 523, 573, 623, 673 and 723 K. The results are shown in Fig. 5b. Upon heating the intensities of the whole spectrum slightly decrease. The peaks at 1440, 1360, 1270 and 1237 cm^{-1} clearly disappear already at relatively low temperature (below 623 K). The 1596 cm^{-1} peak decreases slightly following the increase of temperature. The 1574, 1537, 1208 and 995 cm^{-1} peaks decrease only at high temperature. A significant decrease in the absorbances of the whole spectra takes place above 623 K.

When a gas mixture of about 1100 ppm $NO_2 + 10\%\ O_2$ in He was used and the same procedure was applied similar spectra were observed (not shown). Compared to the

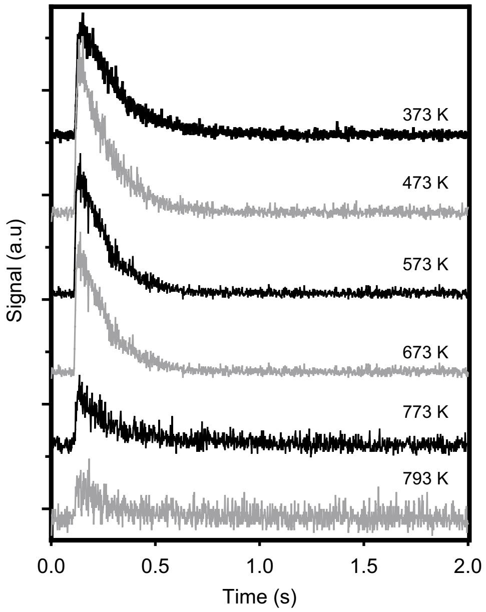


Fig. 6. The pulse responses of 20% O_2/Ar on CeO_2 from 373 to 793 K measured in advanced TAP reactor; pulse size of 1.3×10^{16} molecules.

one exposed to NO_2 only, the assignments slightly shift and become: bridging nitrate (ca. 1600, 1210 and 995 cm^{-1}), bidentate nitrate (ca. 1576, 1265 and 1025 cm^{-1}), monodentate nitrate (ca. 1545, 1234 and 995 cm^{-1}) and chelating nitro compound (1510 and 1265 cm^{-1}). The relative intensity of the bands is slightly higher. Increasing temperature generates the 1360 cm^{-1} peak while diminishing the 1440 cm^{-1} one. The rest of the bands change with the same effect as those with the NO_2 exposed one. The mass spectrometry result of the system is also similar to that of the NO_2 exposed one. Except that during exposure NO emission is lower, while the N_2O signal slowly increases (not shown).

3.3. *Interaction of O_2 with CeO_2; pulse response analysis*

Interaction of O_2 with CeO_2 measured in the advanced TAP equipment is shown in Fig. 6. The figure describes the 200th pulse response of 20 vol.% O_2/Ar through CeO_2 from 373 to 793 K. After 200 pulses at 373 K, the temperature is increased to 473 K in Ar pulses by 5 K/min then 200 pulses of 20 vol.% O_2/Ar were given again. The process is repeated until 793 K. Up to 673 K no strong interaction between O_2 and CeO_2 is observed as the pulse intensities are relatively unchanged. Lowering of the O_2 pulse response intensities is clearly observed at 673 K and higher. Unlike the base lines at low temperatures, which are relatively smooth, at 773 K and 793 K no clear base lines are observed. When an Al_2O_3 sample is used, the interaction with O_2 takes place at temperature higher than 773 K. It should be noted that the response of the Ar pulse with both CeO_2 and Al_2O_3 remains unchanged in shape and delay time as a function of temperature. Only sharp Ar pulse responses were observed under all conditions.

4. Discussion

4.1. *Effect of CeO_2 on NO_2-assisted soot oxidation*

In view of soot oxidation mechanism, the acceleration of soot oxidation should involve intermediates and their decomposition of which the latter is associated with the rate-determining step. In the oxidation of carbon, intermediates are known as Surface Oxygen Complexes (SOC's) [13]. It has been known that for the catalytic oxidation of carbonaceous material with solid catalysts to effectively take place, the three phases (the catalyst, the carbonaceous material and the gas reactant) should be in close contact. In our experimental procedure the soot and CeO_2 are mixed in the so-called loose contact procedure [20]. Either with CeO_2 catalyst or references like Al_2O_3, this type of contact has been shown not to significantly influence the soot oxidation rate in the presence of O_2.

Another way of soot oxidation acceleration is through the formation of reactive gas. This is the principle of using platinum catalyst to oxidise soot under $NO + O_2$ through the formation of NO_2. This NO_2 is very active in the oxidation of soot. It has to be noted that NO alone is non-reactive in the oxidation of soot. Fig. 1 demonstrates the concept. In non-catalysed soot oxidation, the reaction is controlled by C-O_2 reaction. In configuration 3, where NO_2 is generated by platinum catalyst, below 750 K soot oxidation is controlled by C–NO_2 reaction while at higher temperature it is controlled by C–O_2 reaction. This explains the double peak of the oxidation profile. In the following paragraphs, explanation for the acceleration of NO_x-assisted soot oxidation by CeO_2 will be discussed and based on the catalysed formation of reactive gas following NO_2–CeO_2 interaction.

As postulated earlier, one of the possible roles of CeO_2 in the acceleration of soot oxidation in the presence of $NO + O_2$ would be its activity in the oxidation of NO to NO_2. Fig. 1 demonstrates that in the CeO_2-soot configuration, a catalytic effect of CeO_2 in the oxidation of soot exists. Furthermore, in Fig. 2 it is shown that the catalyst is active in the oxidation of NO to NO_2, although Pt is more active. The Pt upstream of CeO_2 configuration has a longer residence time and, therefore, a higher amount of NO_2 is produced.

There is no doubt that this NO_2 will contribute to a higher oxidation rate. The contribution of this additional NO_2 to the oxidation rate is reflected as the oxidation rate of the CeO_2-soot configuration. Since the amount of $CO + CO_2$ from Pt upstream of CeO_2-soot is, however, higher than the sum of Pt upstream of soot and CeO_2-soot configurations, this indicates that besides this additional NO_2 there should be another source that contributes to the higher oxidation rate.

In comparing the oxidation rate of the Pt upstream of soot configuration with physical mixture of Pt-soot configuration [21], the higher oxidation rate of the physical mixture of Pt-soot configuration was explained by the occurrence of the recycle reaction:

$$NO + \frac{1}{2}O_2 \overset{Pt}{\rightleftharpoons} NO_2 \quad (4)$$

$$NO_2 + C \rightarrow CO + NO \quad (5)$$

This reaction network can only partially explain the additional activity because CeO_2 is significantly less active in the oxidation of NO to NO_2 than the platinum catalyst. The effect of CeO_2, in Pt upstream of CeO_2-soot, is, however, in the same order of magnitude with that of Pt in a physical mixture of Pt and soot. For a detailed comparison, one might compare this present study with [21].

As can be concluded from Figs. 1 and 2, below 550 K the amount of NO_2 produced (200–300 ppm) is higher than the amount of $CO + CO_2$ (50–100 ppm). This means that NO_2 does not effectively react with soot at temperature below 550 K and as a result interaction of NO_2 with CeO_2 will take place. Fig. 3 shows that pre-treatment of CeO_2 by NO_2 containing gas increases the soot oxidation activity. CeO_2 gains activity after its exposure at 473 K to NO_2/O_2. Apparently, this activity has to be attributed to NO_2 because exposure to O_2 alone does not affect the activity. This is in agreement with mass spectrometry data of O_2 exposed CeO_2, which showed that no O_2 was observed upon heating. The pulse response experiments confirm that O_2–CeO_2 interaction does not take place below 600 K. Therefore, O_2 exposure at 473 K does not result in oxygen storage on CeO_2.

It is concluded that the acceleration of soot oxidation by CeO_2 is due to the production of active gas desorbed from the cerium (surface) as a consequence of its previous interaction with NO_2. The results of DRIFT analysis coupled with mass spectrometry data discussed in the following section are used to elucidate this hypothesis.

4.2. Interaction of NO_2 with CeO_2

During CeO_2 exposure by NO_2, significant amounts of NO and N_2O were emitted but no O_2 emission was observed. From this stoichiometry it can be concluded that the formation of nitrate as generally postulated is not the only process. As NO_2 is a strong oxidising agent, it is postulated that NO_2 is able to transfer its oxygen to the CeO_2 surface. This oxygen atom is either transformed to oxygen vacant sites of cerium or it forms surface peroxide or super-oxide. Both peroxide and super-oxide are intermediates in O_2 dissociation, leading to the incorporation of gas-phase O_2 into lattice oxygen [22,23]. The reaction of NO_2 with Ce metal centres with oxygen vacancies has been observed by Rodriguez et al. [11] at 300 K based on XANES observation, reaction 2. Clearly, this reaction produces gas phase NO, without O_2 evolution, which is observed during CeO_2 exposure to NO_2 at 473 K. Because N_2O is observed during exposure to NO_2, reaction of NO_2 to N_2O is also one of the processes taking place.

In Fig. 5a several peaks that evolve up to 10 min exposure to NO_2 disappear as exposure time is prolonged. Up to 10 min, the assignments are related to chelating nitro compound (ca. 1500 and 1157 cm^{-1}), monodentate nitrite (ca. 1460 and 1097 cm^{-1}) and nitro compound (ca. 1300 and 1405 am^{-1}). These spectra are similar to the adsorbed species that were observed in the NO exposure to CeO_2 and are generally assigned as surface nitrite species [18]. At 20 min the spectra are similar to CeO_2 exposed to $NO_2 + O_2$ that are generally attributed to surface nitrates [17,24]. The mass spectrometry data confirms this observation. The breakthrough of NO signal takes place after 20 min exposure.

These observations can be explained as follows. At the beginning of NO_2 exposure, the surface contains a high concentration of cerium species with oxygen vacancies. So, interaction of NO_2 with oxygen vacant cerium atoms, reaction (2), is favourable. The NO released is confirmed by TPD-mass spectrometry. Nitro compounds and monodentate nitrite observed in the DRIFT spectra, Fig. 5a, are most likely the intermediates in the oxygen transfer from NO_2 to oxygen vacant cerium on CeO_2 surface. The reaction schemes are postulated in Fig. 7a and b. Ce-□ represents cerium atoms with oxygen vacancies. Bidentate nitrate is postulated to be an intermediate for the peroxide or super-oxide formation, Fig. 7c. All those reactions might take place during NO_2 exposure. Unfortunately there is no IR assignment that gives an indication for the formation of N_2O from NO_2. One of the possible schemes is shown in Fig. 7d. According to this scheme bridging nitrite with assignment at ca. 1260 cm^{-1} [19] and monodentate nitrite should be formed as intermediates.

There are two explanations for the observation that surface nitrates, not surface nitrite, are the dominant species observed. At this stage surface CeO_2 has been covered by ‘surface oxygen’. This adsorbed oxygen might react with surface nitrite formed at the beginning of the exposure to surface nitrate. The second explanation is that cerium atoms with oxygen vacancies are diminished to a large extent, so the interaction of NO_2 with CeO_2 is then more favourable for nitrate formation.

When the temperature programmed experiment was applied, NO_2 is desorbed earlier than NO and O_2. It is difficult to determine from which surface species this NO_2 is evolved. Except for the 1237 and 1505 cm^{-1} couple and the 1360 cm^{-1} peak, which originates from chelating nitro compound and nitrite–nitrato, respectively, the disappearances of other peaks are not clearly related to a particular assignment. For example although the 1237 cm^{-1} peak disappears at low temperature, the 995 and 1537 cm^{-1} peaks still exist up to 723 K, Fig. 5b. These three peaks together are attributed to monodentate nitrate. Furthermore, as already mentioned, the 1360 cm^{-1} is usually attributed to the nitrite–nitrato on the cell window. But since its intensity decreases upon heating, it is suspected that this nitrite–nitrato is formed on CeO_2 surface. It is beyond the scope of this paper to argue whether those phenomena are related to wrong assignment in the research papers of the surface nitrate.

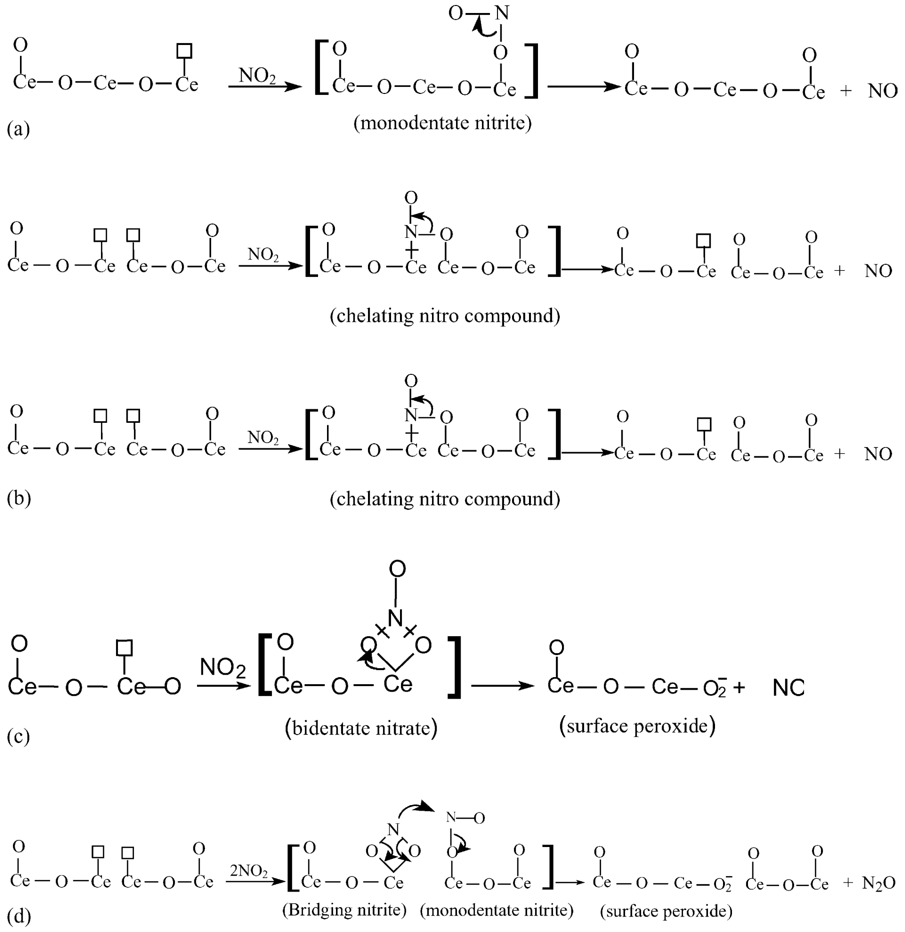


Fig. 7. Reaction scheme showing oxygen transfer from NO_2 to CeO_2.

However, as the intensity of the whole spectra gradually decreases upon heating, this desorbed NO_2 probably resulted from part of the surface nitrate decomposition according to the stoichiometry of reaction (6).

$$Ce(NO_3)_4 \rightarrow CeO_2 + 4NO_2 + O_2 \quad (6)$$

In Fig. 4 it is shown that up to 600 K the emission of NO_2 is not accompanied by O_2. According to reaction (6) nitrate decomposition should also be followed by O_2 emission. A similar effect was observed in the decomposition of surface barium nitrate produced from NO_2 adsorption by BaO [25]. This phenomenon was explained by the formation of barium peroxide instead of barium oxide. Adapting this theory to the present situation, cerium peroxide or super-oxide might be produced during the decomposition of $Ce(NO_3)_4$. In relation to the soot oxidation rate this NO_2 from reaction (6) can contribute to the additional soot oxidation rate.

At higher temperatures, above 600 K, NO and O_2 are emitted simultaneously. In most cases the NO and O_2 curves lie on top of each other. Since there is no indication that surface nitrite is present in the stable spectra, again NO should be emitted from nitrate decomposition, according to reactions (7) and (8).

$$Ce(NO_3)_4 \rightarrow CeO_2 + 4NO_2 + O_2 \quad (7)$$

$$4NO_2 \rightarrow 4NO + 2O_2 \quad (8)$$

If all nitrates decompose to NO the stoichiometry becomes:

$$Ce(NO_3)_4 \rightarrow CeO_2 + 4NO + 3\,O_2 \quad (9)$$

According to reaction (9) the ratio between O_2 to NO has to be 0.75. The fact that in most cases O_2 to NO emission ratio is about one, as shown by overlapping O_2 and NO curves, which is higher than expected by stoichiometry ratio indicates that part of O_2 might be desorbed from other sources. Emission of surface O_2, originated from stored oxygen probably as cerium peroxide and super-oxide as described in the previous paragraph might give an explanation. This oxygen could be a very active species that can again contribute to the higher oxidation rate. The decomposition is very fast in comparison with oxidation rate, as a result no additional NO_x was observed in the flow experiment.

In the process of exposure and flushing of CeO_2 the nitrogen balance is almost close (adsorbed equals desorbed), whereas the oxygen balance revealed that still 90% of oxygen is stored on the CeO_2 either as oxygen surface complexes or as oxygen stored in the bulk. In Table 2 it is shown that about 90% NO_2 is recovered as NO_2, N_2O and NO emissions. This missing nitrate might be retained as bulky nitrate. The coverage that exceeds 100% might indicate the presence of bulky nitrate. The formation of bulky Ce nitrate during desorption could be another reason. These bulky Ce nitrate requires high temperature to decompose. The formation of bulky Ba nitrate was observed in the desorption NO_2 exposed BaO [25]. For oxygen, it is clearly shown that only a small part (10%) of O_2 was recovered by TPD to 723 K. Schlatter and Moitchell showed that in the evacuation of oxygen stored on ceria, only about 5% of the initial oxygen uptake was recovered by evacuation, while 55% of it was recovered when it was reacted with CO [26]. In this experiment evacuation and reaction with CO were done at 773 K for 45 min.

Fig. 3 indicates that at 473 K O_2 exposure to CeO_2 hardly influences the soot oxidation rate with O_2. Heating the O_2 exposed CeO_2 is not followed by O_2 desorption. This means that no activation or oxygen storage takes place on CeO_2 at low temperature, 473 K. This indication is supported by the pulse response data. It is shown that O_2 adsorption by CeO_2 takes place only above 673 K. This conclusion is in agreement with [27,28]. In the present study oxygen storage route initiated by NO_2 in the gas phase has been demonstrated. It is not clear yet if this has the same properties as that from oxygen pulse.

It is interesting to see that above 700 K the NO_2/O_2 pre-treated CeO_2 shows a relatively high oxidation rate. As at this temperature all NO_2 has already desorbed, it is concluded that ‘active oxygen’ instead of NO_2 plays a major role.

The acceleration of soot oxidation by CeO_2 in the Pt upstream of CeO_2-soot can be summarised as followed. The interaction between NO_2 and CeO_2 leads to surface cerium nitrate formation and oxygen transfer to CeO_2. Desorption of surface nitrates generates NO_2 which is very active in the oxidation of soot. The generation of ‘active oxygen’ originated both from nitrate and surface oxygen (peroxide/superoxide) decomposition contributes to the increase of soot oxidation. At the same time NO oxidation by CeO_2 provides additional NO_2 that again increases the oxidation rate. The phenomena of nitrate decomposition to NO_2 and active oxygen desorption were observed in a condition where a step response is applied. In the flow reactor where NO_2 is flown continuously the formation of surface nitrate, surface oxygen and the decomposition thereof take place simultaneously. So, the effect of active oxygen to the oxidation rate could take place continuously. Unfortunately, the emission of 10% N_2O during NO_2 exposure was observed. This will be a serious problem if the system is applied since a new harmful emission, N_2O, is produced. It is well known that N_2O is a powerful green house gas and can also cause depletion of stratospheric ozone.

For the CeO_2 catalyst exposed to $NO_2 + O_2$, the explanation for the relatively high rate of reaction should be similar. In the presence of NO_2/O_2, nitrate formation is more favourable. This is indicated by higher nitrate intensity in DRIFT spectra of the $NO_2 + O_2$ exposed than that of NO_2 exposed. O_2 might also cover part of the CeO_2 surface leading to lower NO_2 interaction with the surface.

In view of practical application, to make use of stored active oxygen and/or decomposition of surface nitrates in the soot oxidation, the buffer capacity of these species should be larger than the trapped soot. This means that a large amount of ceria is needed. Furthermore, the release of the stored ‘active oxygen’ is a slow process in comparison with the desired induced regeneration of the trapped soot.

5. Conclusions

CeO_2 has the potential to accelerate the NO_x-assisted soot oxidation conversion. The interaction of NO_2 with CeO_2 to form initially surface nitrite and nitrate followed by oxygen transfer to the CeO_2 has been demonstrated. This oxygen is stored on CeO_2 and the desorption of it leads to the formation of ‘active oxygen’. This active oxygen is postulated to play an important role in the acceleration of soot oxidation. The desorption of ‘active oxygen’ is a slow process in comparison with the desired soot oxidation. Decomposition of surface nitrate results in gas phase NO_2 that led to a minor effect in soot oxidation. An amount of 10% applied NO_2 is converted into N_2O that might be a serious drawback in the application of ceria as an ‘active oxygen’ storage material.

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