# Effects of O<sub>2</sub> on the Reduction of NO over Prereduced CaO Surfaces: A Mechanistic Understanding

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The effect of  $O_2$  on the reduction of NO over prereduced CaO surfaces is investigated. The experimental results suggest the existence of at least three different reaction channels, of which two are related to the high-temperature reduction of the CaO surfaces and involve the use of extra electrons in breaking the NO bond. The third reaction channel does not employ extra electrons for bond breaking, but the activity is affected by the amount of adsorbed surface oxygens. The difference between the former two reaction channels is found in the temperature needed for an observable activity. The reaction channel which is already active at low temperatures is described by a model based on F-centers, whereas the one which needs elevated temperatures involves a hole transport through the bulk. The activation energy for this transport is determined experimentally using a temperature-programmed reaction technique as well as theoretically by means of ab initio quantum chemistry calculations. Room-temperature exposure to  $O_2$  is suggested to result in a poisoning of the F-centers, but has only a minor effect on the reaction channel proposed for high temperatures. Effects on the reduction of NO of time as well as temperature for the  $O_2$  exposure step are also investigated and found to be consistent with an understanding based on the coexistence of different reaction channels.

#### 1. Introduction

Nitrogen oxides, produced during combustion of fossil fuels, are harmful to the environment. Catalytic materials can be used to effectively reduce them. Several catalytic systems have been commercially available for some years. The three-way catalyst for stoichiometric combustion is one of them. This technique uses supported and promoted Pt to decrease both the  $NO_x$ , CO, and hydrocarbon levels in car exhausts. For stationary power sources selective catalytic reduction by NH<sub>3</sub> over a V<sub>2</sub>O<sub>5</sub>-based catalyst is commonly used. At present, substantial efforts are being made to find an operative system for the reduction of  $NO_x$  by reducing species present in the flue gas under oxygen excess. Supported noble-metal and several zeolite systems have been shown to be efficient in the reduction of  $NO_x$  by hydrocarbons.<sup>1-3</sup> However, the most promising approach is the direct catalytic decomposition of NO to N<sub>2</sub> and O<sub>2</sub>.<sup>4</sup> Several materials have been shown to increase the rate of this reaction, i.e., Cu-ZSM-5,5,6 Sr-Fe oxides,7 perovskite-type compounds,<sup>8,9</sup> and cobalt oxide modified with Ag. One feature, shown by all these materials, is the ability to release oxygen at moderate temperatures.<sup>10</sup>

Although a thorough mechanistic understanding is wanted, it is clear that the detailed activity of each catalyst is system specific. Still, common properties are sought by focusing on the necessary prerequisites for the reduction of NO. This article is part of a series that tries to elucidate the nitrogen chemistry during reduction of NO over alkaline earth oxide surfaces.<sup>11–13</sup> CaO is used as a model substrate to study basic reactions, both by experiment<sup>11–13</sup> and theory.<sup>14–19</sup> In a previous work, correlation was demonstrated between catalytic activity toward the reduction of NO by CO or H<sub>2</sub>, and the impurity content (Na and Fe) of the CaO material.<sup>12</sup> The role of the impurities is to provide electron sinks during the surface oxygen abstraction by the reducing agent. Two models describing this step are currently under debate, i.e., a semiconductor model based on  $O^-$  states in the band gap<sup>12,20</sup> and a model based on F-centers.<sup>21</sup> The oxygen abstraction step creates sites for breaking the N–O bond,<sup>11,12</sup> and a mechanism involving an N<sub>2</sub>O<sub>2</sub><sup>*n*-</sup> intermediate was suggested.<sup>11,19</sup> Furthermore, the effect of the oxygen abstraction step on the subsequent reduction of NO was shown to be independent of the reducing agent, i.e., H<sub>2</sub> or CO.<sup>11</sup> Reduction of NO upon NO adsorption at room temperature and during subsequent heating ramps in Ar was even observed for fully oxidized CaO surfaces.<sup>22</sup> The effect of preadsorbed surface oxygens was examined.

The effect of excess oxygen on the activity of reduced oxide surfaces is investigated. This is done by exposing a prereduced CaO surface to  $O_2$  at different temperatures and measuring the effect on the reduction of NO. The results are compared with the reduction of NO over fully oxidized surfaces. The effects of sequential and simultaneous exposure to O<sub>2</sub> and NO, combined with the discovery of sites accessible only at elevated temperature, result in a comprehensive understanding of the reduction of NO and in the proposition of reaction mechanisms involving both semiconductor properties and F-centers. The former sites are discussed to be the ones involved in a reaction channel operative at high temperature, whereas the latter are involved in a reaction channel which is already active at low temperature. Ab initio quantum chemistry calculations are used to further develop the understanding of the semiconductor model in terms of a hole hopping mechanism for charge transport.

#### 2. Experimental Section

A fixed bed reactor connected to a quadropole mass spectrometer (QMG 421 of Balzers) was used. The quartz reactor

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(i.d. 22 mm, length 500 mm) had an asymmetric construction to avoid heating the upper metal fitting and the vacuum-tight Viton O-ring. Gas sampling was done by a quartz capillary 2 mm under the bed supporting a sintered quartz filter. The temperature was measured with a K-type thermocouple 3 mm under the tip of the capillary, avoiding any interference in the results due to its catalytic activity. The heating ramps were controlled with a second thermocouple in contact with the heating coil.

The bed material investigated consisted of 0.750 g of CaO (Fisher Scientific) mixed with 1 g of quartz sand, pro analysi (Merck), and was placed on a sintered quartz filter in the reactor. The quartz sand was added to reduce the pressure drop. The gases used were 5000 ppm NO, 3000 ppm isotope-labeled <sup>15</sup>NO, 5000 ppm H<sub>2</sub>, and 10% O<sub>2</sub>, all in Ar. The flows were controlled by mass flow controllers (Brooks, type 5850E) to a flow rate of about 20 mL/min (293 K, 1 bar), unless stated otherwise. The bed material had been heat treated overnight at 800 °C in an Ar flow and was then exposed to H<sub>2</sub> at this temperature for 15 min. This reducing step was repeated after every experiment.

In addition, quantum chemistry calculations were performed in order to clarify basic features of the semiconductor model. An embedded cluster model was employed, where three atoms are described explicitly and the rest by point charges or projection operator dressed point charges. The latter are used to mimic the effect of Pauli repulsion toward the inert  $Ca^{2+}$  ion cores. The all-electron descriptions of the linear  $[O-Ca-O]^{-1}$  unit, which is taken to accommodate one hole, uses the 4s 3p 1d and 5s 4p atomic natural orbitals descriptions<sup>23</sup> for oxygen and calcium, respectively. The calculations were performed by means of a Coulomb hole augmented restricted open-shell Hartree–Fock method.<sup>24,25</sup> The overall reliability of similar embedded cluster schemes has been shown in previous studies.<sup>16,19</sup>

#### 3. Results

3.1. O<sub>2</sub> Treatment at Room Temperature–Effects on the Reduction of NO. In a first series of experiments, the roomtemperature stability of the sites induced by the prereduction step were investigated by exposing the bed material to a gas flow of 5.2% O<sub>2</sub> in Ar. The effect of the intermediate exposure to O<sub>2</sub> on the activity of the substrate toward the reduction of NO is examined after the reactor was flushed by Ar to evacuate remaining O2. The bed material was therefore exposed to a gas flow of NO (2400 ppm) for 15 min while the reactant, NO, as well as possible reaction products, N<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>O, were monitored by the mass spectrometer. Oxygen exposure times between 0 (no intermediate O<sub>2</sub> exposure) and 120 min were investigated. The results are shown in Figure 1. In the absence of any O<sub>2</sub> treatment, a transient formation of N<sub>2</sub>, followed by a transient formation of N<sub>2</sub>O, is observed. The N<sub>2</sub> peak is due to a reaction channel for complete reduction of NO. The reduction capacity of the CaO substrate diminishes after about 180 s and the further reduction of NO becomes incomplete, i.e., a partial reduction of NO to N<sub>2</sub>O. Intermediate exposure of the reduced substrate to O<sub>2</sub> causes the formation of N<sub>2</sub> to disappear. Only the reaction channel for partial reduction remains. Increased O<sub>2</sub> exposure time results in a decreased formation of N<sub>2</sub>O. No O<sub>2</sub> formation was observed in any of the experiments.

The bed material was then exposed to a heating ramp up to 800 °C. This was done in a flow of Ar, using a heating rate of 0.5 K/s. In Figure 2a, the formation of  $N_2O$  is plotted versus ramp temperature for the different  $O_2$  exposure times. A decrease



Figure 1. Room-temperature  $N_2O$  formation during exposure of a prereduced CaO surface to NO: effect of intermediate  $O_2$  exposure at room temperature.



**Figure 2.** Formation of  $N_2O$  (a) and  $N_2$  (b), as well as NO desorption (c) during the successive heating ramps in Ar: effect of intermediate  $O_2$  exposure at room temperature.

in N<sub>2</sub>O formation is observed with increasing  $O_2$  exposure time. The same trend is observed for the formation of N<sub>2</sub> (Figure 2b). The results show the existence of reaction channels which



Figure 3. N<sub>2</sub> formation during exposure to NO at 800 °C: effect of intermediate  $O_2$  exposure at room temperature.



Figure 4. Room-temperature  $N_2O$  formation during exposure of a prereduced CaO surface to NO: effect of intermediate exposure to  $O_2$  at 30, 170, and 380 °C.

were not easily accessible at room temperature. Formation of N<sub>2</sub>O is found at temperatures between 50 and 425 °C with a maximum at about 150 °C independent of O<sub>2</sub> exposure time. N<sub>2</sub> is formed between 60 and 700 °C. The corresponding desorption of NO is shown in Figure 2c. Two desorption peaks, a low (135 °C)- and a high-temperature (430°) peak, are observed. The low-temperature desorption peak is not influenced by the intermediate exposure to O<sub>2</sub>. This is not the case for the high-temperature peak, i.e., an increased O<sub>2</sub> exposure time results in an increased NO desorption. This could be related to the decreased amount of NO that is reduced to N<sub>2</sub>.

After the heating ramp experiments, the bed materials were reexposed to NO at 800 °C (same gas mixture as previously). The transient formation of N<sub>2</sub>, seen in Figure 3, demonstrates the presence of sites that were not reoxidized during the previous treatment and thus in a reaction channel only accessible at elevated temperatures. No formation of N<sub>2</sub>O is observed at 800 °C. This is expected since CaO is known to catalyze the decomposition of N<sub>2</sub>O.<sup>18</sup> Interesting is the slow decrease in the formation of N<sub>2</sub> with increasing O<sub>2</sub> exposure time.

**3.2.** O<sub>2</sub> **Treatment at Elevated Temperature–Effects on the Reduction of NO.** In these experiments the effect of an intermediate O<sub>2</sub> exposure was investigated at 30, 170, and 380 °C, while the O<sub>2</sub> exposure time was kept at 15 min. The bed was first cooled in Ar to 30 °C before exposing it to NO for the two latter O<sub>2</sub> exposure temperatures. N<sub>2</sub>O was the only reaction product formed at room temperature. In Figure 4 the N<sub>2</sub>O formation is displayed versus time for the three investigated O<sub>2</sub> exposure temperatures. A decrease is observed with increasing temperature. After exposure to NO, the bed materials were heated under an Ar flow to 800 °C. In Figure 5a the transient N<sub>2</sub>O formation is plotted versus ramp temperature. A maximum



**Figure 5.** Formation of  $N_2O$  (a) and  $N_2$  (b), as well as NO desorption (c) during the successive heating ramps in Ar: effect of intermediate exposure to  $O_2$  at 30, 170, and 380 °C.

is observed at about 150 °C and the amount decreases with increasing O<sub>2</sub> exposure temperature. The low-temperature formation of N<sub>2</sub> disappears for the exposure temperatures of 170 and 380 °C (Figure 5b). The high-temperature N<sub>2</sub> formation is also affected by the O<sub>2</sub> exposure temperature, i.e., the amounts decrease with increasing exposure temperature. The formation of N<sub>2</sub> for an intermediate O<sub>2</sub> exposure at 380 °C differs from the others, i.e., the peak temperature is shifted to higher temperatures. This effect is correlated to a third NO desorption peak as can be observed in Figure 5c. In this figure, the desorption of NO is displayed versus the ramp temperature. This third desorption peak is accompanied by an O2 formation and is ascribed to the desorption of an -NO2 intermediate (see below). It is interesting to note that increased O2 exposure temperatures result in a decreased NO desorption. This is the opposite of what was observed by increasing the time of O2 exposure.

The bed material was then reexposed to NO at 800 °C. A transient formation of  $N_2$  is seen in Figure 6 for all  $O_2$  exposure temperatures, demonstrating the presence of sites that were not reoxidized during the  $O_2$  treatment. The amount of formed  $N_2$  decreases with increasing intermediate  $O_2$  exposure temperature. The unexpected robustness of this high-temperature channel to  $O_2$  exposure is intriguing and was therefore the subject for further investigation. The temperature at which it is active



**Figure 6.** N<sub>2</sub> formation during exposure to NO at 800 °C: effect of intermediate exposure to  $O_2$  at 30, 170, and 380 °C.



**Figure 7.** Formation of  $N_2$  during heating ramps in NO for a prereduced CaO: effect of intermediate exposure to  $O_2$  at 30, 170, and 380 °C.



Figure 8. Formation of  $N_2$  during exposure of a prereduced CaO surface to a mixture of NO and  $O_2$  at 600 and 800 °C, respectively.

toward the reduction of NO can be determined by performing a heating ramp in an NO-containing atmosphere (1200 ppm) instead of Ar. The total gas flow was only 12 mL/min during this experiment. A transient N<sub>2</sub> production was observed in a temperature interval between 500 and 800 °C as is shown in Figure 7. In this figure, the N<sub>2</sub> formation is plotted versus time, not versus temperature, since not all the sites were reoxidized upon reaching the final ramp temperature. The formation of N<sub>2</sub> was accompanied by a corresponding decrease in the NO signal (not shown), confirming the actual reduction of NO. The amount of N<sub>2</sub> formed is highest for an O<sub>2</sub> exposure temperature of 30 °C and decreases with increasing O<sub>2</sub> exposure temperatures, as expected. A maximum N<sub>2</sub> formation is found at about 760 °C for all three O<sub>2</sub> exposure temperatures.

Exposure of the bed material simultaneously to NO (2700 ppm) and  $O_2$  (9700 ppm) at 600 and 800 °C, respectively, results in a transient  $N_2$  formation (Figure 8). Formation of neither  $N_2$  nor  $N_2O$  was observed for exposures at 30, 200, or 400 °C. However, the formation of small amounts of  $N_2$  is observed during the succeeding heating ramp in a gas mixture containing



**Figure 9.** Desorptions of NO and  $O_2$  during a heating ramp in a mixture of NO and  $O_2$  mixture for a prereduced CaO surface.



**Figure 10.** Formation of  $N_2O$  at 30 °C (a), as well as  $N_2$  during the preceding heating ramp in Ar, (b) for an oxidized CaO surface exposed to NO at room temperature.

both NO and O<sub>2</sub>. In Figure 9, the corresponding NO and O<sub>2</sub> signals are shown versus the ramp temperature. Two types of NO desorption peaks can be seen: a low-temperature peak which is due to preadsorbed NO and a high-temperature peak which is likely to be due to a  $-NO_2$  intermediate, as can be concluded by correlating the NO desorption and the O<sub>2</sub> formation. The gas flow for these experiments was 15 mL/min.

**3.3. Reduction of NO over an Oxidized CaO Surface.** In this experiment the activity of an oxidized CaO surface toward the reduction of NO was investigated. The bed material was exposed to a gas flow of NO (2400 ppm) at 800 °C for 15 min and cooled in Ar to room temperature. The bed material was then reexposed to NO (2400 ppm) for 15 min and the formation of possible reaction products (as  $N_2$  and  $N_2O$ ) was monitored. A transient production of  $N_2O$  is observed (Figure 10a). Finally the bed material was heated to 800 °C under a flow of Ar. The  $N_2$  and  $N_2O$  formations are displayed versus ramp temperature in Figure 10b, where a temperature dependence in the formation of  $N_2$  and  $N_2O$  consistent with that displayed in Figures 1 and 2b is found.

**3.4. Kinetics.** Equations relating Arrhenius kinetic parameters A and  $E_a$  (preexponential factor and apparent activation energy, respectively), surface coverage  $\theta$ , and linear heating rate ( $\beta$ ) have been reviewed by Lord and Kittelberger.<sup>26</sup> It was shown that the slope of a plot of  $\ln(T_m^2 \theta_m^{n-1}/\beta)$  versus  $1/T_m$  reproduces the apparent activation energy for desorption by multiplying it with the gas constant R. T<sub>m</sub> represents the temperature of maximum desorption,  $\theta_{\rm m}$  the peak coverage, and *n* the order of the desorption reaction. In the present work, *n* will be taken as one. This simplifies the plot to  $\ln(T_m^2/\beta)$  versus  $1/T_m$ . Calculations have shown that the assumption of a reaction order of 1 does not introduce major errors in the activation energy.<sup>26</sup> The activation energy for reduction of NO in the high-temperature channel is determined by exposing a reduced CaO surface to NO (2500 ppm) during a heating ramp between room temperature and 900 °C, while measuring the formation of  $N_2$ . Repeating this for different heating rates ( $\beta$ ) results in an activation energy for the reduction of NO to N<sub>2</sub> of about 25 kcal/mol.

#### 4. Discussion

The effect of  $O_2$  on the reduction of NO over prereduced CaO surfaces is investigated and the resistance toward poisoning by  $O_2$  is shown to depend on the set up of the experiments, i.e., sequential (Figures 1–7) or simultaneous (Figures 8 and 9) exposure to  $O_2$  and NO. The role of a prereduction has been discussed before<sup>11,12</sup> and results in a surface oxygen abstraction, depositing the electrons of the abstracted oxygen ion in the substrate. The fate of these electrons is not clear, and two models are under consideration. One is based on a semiconductor model using impurity states in the band gap as electron acceptors, whereas in the other model the excess electrons are localized in F-centers. An activation energy for the oxygen abstraction step of about 25 kcal/mol was found.<sup>11</sup>

A common feature in the results of the sequential roomtemperature exposure to O2 and NO is that some sites are inaccessible until elevated temperatures (Figure 3). For heating ramps in NO (Figure 7), a maximum reduction is observed at about 760 °C (heating rate of 0.5 K/s). Thus, even in the presence of an oxidant (NO), the reduced CaO is not fully oxidized until elevated temperatures. The sites involved in the high-temperature reduction of NO will be referred to as the "high-temperature sites" and a reaction channel based on an activated hole transport is proposed to explain their activities. This understanding results from three independent observations, i.e., (i) an apparent activation energy of 25 kcal/mol for the surface oxygen abstraction,11 (ii) an apparent activation energy of 25 kcal/mol for formation of N2 under heating ramps in NO (results presented in this paper), and (iii) a maximum apparent activation energy of 10 kcal/mol for the breaking of a NO bond in the presence of excess electrons.<sup>11</sup> These experimental results indicate that the transport of holes might be the rate-determining step, i.e., a transport of holes from the O<sup>-</sup> species to the surface during the oxygen abstraction step and back during the reoxidation.

This understanding would explain the correlation between apparent activation energy for the reduction of NO by  $H_2$  and the lattice parameter of the respective alkaline earth oxides. In previous work,<sup>12</sup> an increase in apparent activation energy with lattice parameter, and thus with increasing ionic radii of the alkaline earth cation, was found. This is in full agreement with the mechanism presented here. An increased lattice constant results in a decreased overlap between the oxygen orbitals and consequently in hole localization and thus in increasing the apparent activation energy for hole transport.

The effect of lattice parameter on the hole hopping mechanism for charge transport is illustrated semiquantitatively by employing a regularized Hartree-Fock method.<sup>24,25</sup> The activation energies are taken to be reflected in the relative stabilities of the symmetry broken odd-electron system O<sup>-</sup>-Ca<sup>2+</sup>-O<sup>2-</sup> embedded cluster<sup>16,19</sup> and the symmetric system, which delocalizes the hole over the two oxygen ions. Activation energies in the range 20-32 kcal/mol are obtained by simply varying the lattice constant in the range of the alkaline earth oxide series from MgO to BaO. The activation energy for holes hopping in CaO is determined to be 26.2 kcal/mol. It is gratifying to note the semiquantitative agreement with the apparent activation energies for NO reduction on these substrates.<sup>12</sup> This was expected on the basis of experience with similar systems.<sup>14–16</sup> The main sources of error are due to the rigid cluster ansatz, the assumption that nearest-neighbor interactions in an external electrostatic potential determines the charge carrier properties of the alkaline earth oxides, use of an effective electron correlation description, and neglect of dispersion interactions. The potential for such a model in explaining experimental observations relies on the cancellation of errors. In this respect the objective to seek the possible origin for a trend in an activation energy is ideal. This is why the somewhat fortuitous agreements between experiment and theory, regarding both trend and magnitudes, can be taken to support the existence of a hole transport controlled reaction channel for doped alkaline earth oxides.

A semiconductor model based on an apparent activation energy of 25 kcal/mol for hole transport cannot explain the reduction of NO at room temperature since for the reduction of NO at these temperatures a much lower activation energy is expected. Figure 1 shows the transient formation of N2 and N2O during exposure of the CaO surface to NO at room temperature. A significant difference is observed in the reduction of NO with and without an intermediate O<sub>2</sub> exposure, i.e., a reduced NO reduction capacity and a disappearance of the N<sub>2</sub> formation. Increasing the O<sub>2</sub> exposure time results in a further decrease of the N<sub>2</sub>O formation. The activity at these low temperatures is complicated and can best be explained by a combination of two reaction channels of which only one involves extra electrons. These extra electrons must be easy to access, which makes electrons localized in F-centers possible candidates. The nature of these has been extensively reviewed in the literature.<sup>21,27-29</sup> An intermediate room-temperature exposure to O<sub>2</sub> would stabilize the electrons of the F-center by forming peroxides and/ or superoxides. These sites, involved in a reaction channel accessible at low temperatures and referred to as the "lowtemperature sites", are thus expected to be eliminated by an exposure of the substrate to O2. Left is then the activity observed after the intermediate exposure to O<sub>2</sub>. At this stage there are no electrons localized in F centers available and the activation energy for hole transport is too high to have a significant participation. A third reaction channel which does not involve transport of holes and/or F centers and of which the effectiveness decreases with increasing O<sub>2</sub> exposure time is therefore needed. Such a reaction channel has been proposed by Platero et al.<sup>30</sup> and Cerruti et al.31 for MgO surfaces, based on infrared spectroscopy studies:

$$4NO + 2O^{2-} \Rightarrow 2NO_2^{-} + N_2O_2^{2-}$$
 (R1)

$$N_2 O_2^{2-} \Longrightarrow N_2 O + O^{2-}$$
(R2)

It is gratifying to notice that even in the absence of a surface oxygen abstraction step the reaction mechanism, as proposed



Figure 11. Activation energy determination for the reduction of NO over the high-temperature sites.

#### prereduced CaO

#### (excess electrons)

two reaction channels eploiting the substrate activity

surface property: F-centers

active at low temperatures

bulk property: hole transport active at high temperature

#### no pretreatment

### small overall activity at low temperature

Figure 12. A schematical overview of the respective reaction channels.

by Platero et al.<sup>30</sup> and Cerruti et al.,<sup>31</sup> is based on the same type of intermediate,  $N_2O_2^{n-}$ . However, the probability of its formation in the absence of excess electrons is expected to be much lower. The activity of unreduced surfaces has also been addressed by Yanagisawa<sup>32</sup> and was again explained by the formation of an (NO)<sub>2</sub> intermediate, providing the necessary N–N bond.

A schematic overview of the respective reaction channels is given in Figure 12.

Even after an exposure to  $O_2$  for 120 min, the amount of  $N_2O$  formed exceeds that observed for fully oxidized surfaces (Figures 1 and 10.a). One possible explanation is that this activity is not associated with the activity for fully (high temperature) reoxidized surfaces and thus should include a different type of site. This site could be related to the presence of impurities close to the surface. Another possible explanation is the poisoning of the  $N_2O$  formation by adsorbed surface oxygens. This effect has been observed in a previous work,<sup>22</sup> i.e., the presence of adsorbed surface oxygens deteriorates the  $N_2O$  formation upon NO exposure at room temperature. Extrapolation to the here presented results would suggest a decrease in  $N_2O$  formation with increasing  $O_2$  exposure time to result from an alteration of the surface by adsorbed surface oxygens.

Increasing the temperature by a heating ramp in Ar affects the substrate. All oxygens that were adsorbed during the  $O_2$ exposure, altering the surface and responsible for the decreased  $N_2O$  formation at room temperature, will be integrated in the crystal structure since no  $O_2$  desorption was observed at any time. This integration involves the formation of  $O^{2-}$  ions by the adsorbed oxygen species and thus implies the involvement of a hole transport. The higher the temperature, the faster this effect. The decreased  $N_2$  formation at 800 °C with increasing  $O_2$  exposure time confirms such an electron consuming mechanism, although the latter effect can also partially be due to an increased NO reduction during the heating ramp the lower the intermediate  $O_2$  exposure time. The effect of this is expected to be low since the activation energy of hole transport has been shown to be high.

Increasing the  $O_2$  exposure temperature results in a decreased formation of N<sub>2</sub>O at room temperature and of N<sub>2</sub>O and N<sub>2</sub> during heating ramps. The formation of N<sub>2</sub> during NO exposure at 800 °C is also significantly decreased with increasing O<sub>2</sub> exposure temperature, resulting in fewer high-temperature sites. This is suggested to be related to an increase for the rate of O-O bond dissociation and for surface diffusion of oxygen species with increased  $O_2$  exposure temperature. The results indicate that a temperature of 400 °C is sufficient for a significant O<sub>2</sub> dissociation and peroxide formation, besides the ones due to O<sub>2</sub> adsorption at F-centers. Evidence for this is found in the high-temperature NO desorption peak in Figure 5c. This desorption is ascribed to the desorption of an NO<sub>2</sub> intermediate, while the second oxygen of the peroxide remains at the surface as an O<sup>n-</sup> species consuming the electrons contained in the impurity-induced sites, and decreasing the amount of electrons available for NO bond breaking.

Simultaneous exposure to  $O_2$  and NO of the reduced CaO surface results in the disappearance of the formation of  $N_2$  and  $N_2O$  for exposure at room temperature, 200 and 400 °C, whereas a transient  $N_2$  formation was observed during heating ramps. Exposure at 600 and 800 °C results in the formation of  $N_2$  (Figure 8). The high-temperature sites are shown once more to be quite stable. The results suggest, for the lower temperatures, the formation of an intermediate from reaction between NO and  $O_2$  inhibiting the formation of  $N_2$  and/or  $N_2O$ .

### 5. Conclusions

The presented results comprise basis for the development of a mechanistic understanding of the NO reduction by H<sub>2</sub> or CO over CaO surfaces at temperatures above 500 °C. The apparent activation energy for the overall reaction was determined to be 26-27 kcal/mol and independent of impurity content or reducing agent.<sup>12</sup> This value was ascribed to the surface oxygen abstraction step (about 25 kcal/mol). The reduction of NO by the high-temperature sites is also found to display an activation energy of 25 kcal/mol. The similarity between the three activation energies suggests that the rate-determining step in the overall reaction is the transport of holes through the bulk. Further support is found by ab initio quantum chemistry calculations. The presence of low-temperature sites is further substantiated and ascribed to F-centers. These do not affect the overall reaction, since the formation of F-centers is believed to have a higher activation energy than 25 kcal/mol. The third type of sites does not involve a previous surface oxygen abstraction, but the intermediate involved is the same, N<sub>2</sub>O<sub>2</sub><sup>n-</sup>. The probability of its formation is, however, much lower in the absence of excess electrons and does not appear above 500 °C. It can therefore be omitted in the final reaction mechanism.

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