Elementary Steps of the Catalytic NO_x Reduction with NH₃: Cluster Studies on Reaction Paths and Energetics at Vanadium Oxide Substrate

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ABSTRACT

We consider different reaction scenarios of the selective catalytic reduction (SCR) of NO in the presence of ammonia at perfect as well as reduced vanadium oxide surfaces modeled by V₂O₅(010) without and with oxygen vacancies. Geometric and energetic details as well as reaction paths are evaluated using extended cluster models together with density-functional theory (DFT). Based on earlier work of adsorption, diffusion, and reaction of the different surface species participating in the SCR we confirm that at Brønsted acid sites (i.e. OH groups) of the perfect oxide surface nitrosamide, NH₂NO, forms a stable intermediate. Here adsorption of NH₃ results in NH₄ surface species which reacts with gas phase NO to produce the intermediate. Nitrosamide is also found as intermediate of the SCR near Lewis acid sites of the reduced oxide surface (i.e. near oxygen vacancies). However, here the adsorbed NH₃ species is dehydrogenated to surface NH₂ before it reacts with gas phase NO to produce the intermediate. The calculations suggest that reaction barriers for the SCR are overall higher near Brønsted acid sites of the perfect surface compared with Lewis acid sites of the reduced surface, examined for the first time in this work. The theoretical results are consistent with experimental findings and confirm the importance of surface reduction for the SCR process.

1. INTRODUCTION

The removal of NO_x species from exhaust emissions is a fundamental challenge in environmental catalysis¹. Here the selective catalytic reduction (SCR) of NO_x by ammonia is widely used to remove the NO_x according to

or

The SCR process is also of great industrial importance as it is used in large stationary sources such as fossil-fuel power plants to dispose of NO_x. At present, TiO₂-supported V₂O₅-WO₃ and TiO₂-supported V₂O₅-MO₃ catalysts are predominantly applied in industrial applications and continue to be developed further¹⁻⁷.

Due to its importance, the SCR reaction has been the subject of various experimental as well as theoretical studies, see Ref. 7 and references therein. It is generally agreed⁷ that under dilute reaction conditions (a) the reaction proceeds according to eq. (1) where NO is the reactant and not NO₂, (b) N₂O does not appear as an intermediate, (c) the resulting N₂ species consists of one nitrogen of the initial NO and one of NH₃, and (d) the reaction mechanism is of redox type, where O₂ oxidizes the surface sites that get chemically reduced by other reactants. It is claimed that the redox reaction proceeds according to a Mars-van-Krevelen mechanism⁸ where the catalyst gets chemically reduced by the formation of oxygen vacancies^{7,9}. Most of the reaction mechanisms suggested by experimentalists assume that NO from gas phase or a weakly bound state reacts with NH₃ that is adsorbed at the catalyst surface⁷. Further, experimental studies have identified two different surface species after ammonia adsorption. First, surface ammonium ions, NH₄⁺ are believed to be the outcome of NH₃ adsorption at surface OH groups (Brønsted acid sites) which result from previous surface reactions^{10,11}. Second, ammonia is assumed to adsorb near vanadium centers (Lewis acid sites), a species that is often denoted as “coordinated ammonia”^{10,11}. Thus, both Lewis and Brønsted acid sites need to be considered in the SCR process. In contrast to experimental results previous theoretical studies investigating NH₃ adsorption at the perfect V₂O₅(010) surface could only verify the presence of one strongly bound NH₄⁺ species¹²⁻¹⁹. Obviously, important details of the reaction mechanism have not yet been unveiled and essential questions, e.g. the actual nature of the active site, are still under debate. Therefore, further theoretical and experimental efforts are necessary to understand the SCR reaction mechanism.

In previous studies considering elementary reaction steps that have been discussed so far⁷ we divided the SCR reaction into three parts^{20, 21}

- (i) The initial interaction and adsorption of gas phase NH_3 and NO resulting in different reaction species at the catalyst surface. Here relative surface binding energies of the adsorbate species have important implications for possible reaction mechanisms.
- (ii) Dehydrogenation and hydrogenation of NH_x surface species, surface water and oxygen vacancy formation which contribute to the reaction. These processes are accompanied by adsorbate as well as surface oxygen diffusion.
- (iii) Interaction of the different adsorbates with the NO near the surface involving bond breaking / making and resulting in different reaction paths. Here possible reaction scenarios can be already suggested by the findings in (i), (ii).

In our preceding theoretical studies^{20, 21} we focused on parts (i) and (ii) of the reaction. We could show that the adsorption and surface diffusion of hydrogen significantly facilitates the formation of oxygen vacancies, of surface water and possible water desorption²¹. Thus, it is very likely that oxygen vacancies occur under reaction conditions and provide reduced surface sites. Further, we investigated the adsorbate binding of different species at the vanadium oxide surface²⁰. This includes hydrogen, nitrogen, NO , ammonia, as well as NH_x species, $x = 1, 2, 4$ generated by (de)hydrogenation processes at the surface. Going beyond previous theoretical studies by others¹²⁻¹⁹ where only sections of the perfect $\text{V}_2\text{O}_5(010)$ surface have been examined, we considered also models for sections of the reduced surface due to oxygen vacancies. Our theoretical study showed that surface reduction strongly affects the adsorption properties and reduced sites may play an important role for the SCR reaction. In particular, the presence of NH_3 surface species stabilizing near Lewis acid sites, so called “coordinated ammonia”, can be explained only by considering reactive vanadium sites, such as those near oxygen vacancies²⁰. Further we could show that surface reduction facilitates the dehydrogenation of NH_3 to form $(\text{NH}_2 + \text{H})$ ²¹ as suggested in the ‘amide-nitrosamide’ SCR reaction mechanism proposed earlier²².

In the present study we focus on part (iii) which deals with the interaction of the different adsorbates with NO resulting in different reaction paths. Mass spectroscopic data obtained during the reaction of NH_3 with NO on vanadium oxide catalysts indicate that nitrosamide, NH_2NO , is the key intermediate²³. Further, theoretical investigations showed that the reaction of NO with NH_2 to yield N_2 and H_2O proceeds in gas phase via the NH_2NO intermediate^{24, 25}. Moreover, NH_2NO was

identified as intermediate in most of the theoretical studies investigating the SCR reaction at V_2O_5 surfaces as well as at V_2O_5 films on TiO_2 support^{12, 15, 17, 19, 26, 27}. On the other hand, previous theoretical studies have shown that NH_2NO formed at the $V_2O_5(010)$ surface can decompose to molecular N_2 and H_2O with fairly small energy barriers^{12, 15}. Thus, this decomposition will not be considered in the present work and we restrict ourselves to catalytic reaction steps starting from gas phase NO and NH_3 resulting in the NH_2NO intermediate at the support. Here we compare the formation of NH_2NO near Lewis acid sites with that near Brønsted acid sites. So far, theoretical studies that considered perfect V_2O_5 surfaces as substrate focused on reactions at Brønsted acid sites^{12, 15, 17, 19} while only one study addressed the reaction near Lewis acid sites¹⁷. They found that near Lewis acid sites of the perfect surface ammonia adsorbs only weakly and the dehydrogenation to form NH_2 is highly endothermic¹⁷. As a result, this study does not confirm important steps of the ‘amide-nitrosamide’ reaction mechanism²² and the formation of NH_2NO near Lewis acid sites is found to be energetically unfavorable¹⁷. We showed previously that Lewis acid sites of the reduced surface are more reactive for the adsorption of ammonia as well as for the dehydrogenation to form NH_2 ^{20, 21}. This suggests the importance of these sites for the SCR reaction as will be discussed below in great detail.

In Section 2 we introduce our catalyst surface models and discuss computational methods used in this work while Section 3 presents results and discussion. Finally, Section 4 summarizes our conclusions.

2. THEORETICAL DETAILS

In the following, the local surface models applied in this study and corresponding theoretical methods will be discussed only briefly. A more detailed account is presented elsewhere^{20, 21, 28}.

2.1. Geometry and cluster models

Local environments of the vanadium oxide catalyst substrate are modeled by sections of the ideal orthorhombic vanadium pentoxide, V_2O_5 , bulk at its (010) surface²⁹ whose structure is well characterized²⁹⁻³¹. Here clusters of different size and shape cut out from V_2O_5 bulk are considered as

model substrates where dangling V-O bonds at the cluster periphery are saturated by hydrogen atoms positioned along the virtual O-V bond direction at a distance of 0.99 Å^{20, 21, 28}. In this work we focus on results for the V₁₀O₃₁H₁₂ substrate cluster, see Fig. 1, which offers all differently coordinated surface oxygen sites, singly, doubly, and triply coordinated O(1), O(2), O(3), and is in its size a compromise between simulation accuracy and computational effort. This cluster approach was used rather successful in earlier investigations of vanadium and other transition metal oxide substrates, such as MoO₃³².

Here we consider two different possible reaction sites at the V₂O₅(010) surface, *Brønsted* acid sites, which are modeled by OH groups resulting from hydrogen pre-adsorbed at oxygen sites of the perfect surface, and *Lewis* acid sites, simulated by vanadium near oxygen vacancies of the surface. Starting from the perfect substrate cluster V₁₀O₃₁H₁₂, this suggests for a Brønsted site a model cluster V₁₀O₃₁H₁₂H where the OH group is formed with the singly coordinated oxygen O(1) near the cluster center, see Fig. 1a. On the other hand, a Lewis site can be modeled by a surface vanadium site near the vacancy of singly coordinated oxygen O(1) at the center of a V₁₀O₃₀H₁₂ vacancy cluster, see Fig. 1b. These model clusters form the basis of the present calculations²⁸.

2.2. Electronic structure and energetics

The electronic structure of the present clusters is evaluated employing density functional theory (DFT) as implemented in the cluster code StoBe³³ using Gaussian basis sets of double zeta valence plus polarization (DZVP) quality, for further basis set details see²⁰. Electron exchange and correlation is accounted for by the gradient corrected revised Perdew, Burke, and Ernzerhof (RPBE) functional³⁴⁻³⁶ as introduced by Hammer et al.³⁷. Geometric configurations of clusters representing initial and final reaction states as well as stable intermediates are evaluated in total energy minimizations including reactants and corresponding substrate atoms. The latter account for surface relaxation where the two central vanadyl units and the connecting bridging oxygen of the surface clusters, see Fig. 1, are considered flexible. Cluster ground states with spin multiplicity other than singlet are obtained by spin polarized calculations. For clusters with an even number of electrons we compared the equilibrium structures at the potential energy surfaces (PES) with multiplicity 1 with those for multiplicity 3. Here triplet states were found to be energetically favorable in all cases. Therefore, we restrict our discussion of possible reaction paths to the PES related to triplet states.

Transition states along corresponding reaction paths are located using the dimer³⁸ and the nudged elastic band (NEB) method³⁹⁻⁴¹. At least seven images are used to model the minimum energy path and the climbing image modification of the NEB algorithm⁴² was employed to evaluate the corresponding transition state. Both methods are based on first order derivatives. Therefore, the saddle points on the potential energy surface characterizing transition states are verified by subsequent vibrational analyses.

Energetic details of the different SCR reaction steps are discussed on the basis of total energies where all corresponding reactant molecules are included with the relaxed substrate cluster. This means, in particular, that at the initial state the NH₃ and NO molecules in gas phase are accounted for by their total energies at the optimized free molecule geometry while the catalyst substrate is included by the total energy of the appropriately optimized cluster shown in Fig. 1. The sum of all energies of this initial state, E_{initial} , is then taken as the reference to characterize different reaction steps. Thus, relative reaction energies ΔE_i of a given intermediate equilibrium or transition state i are described by total energy differences

$$\Delta E_i = E_{\text{tot}}(\text{catalyst} + \text{reactants at step } i) - E_{\text{initial}} \quad (3)$$

where positive / negative ΔE_i values refer to endothermic / exothermic reaction steps. Further methodological details are discussed in^{20, 21, 28}.

3. RESULTS AND DISCUSSION

In the following, we consider an important part of the selective catalytic reduction, the formation of the nitrosamide intermediate from gas phase NO and NH₃. Here two reaction scenarios involving different catalytic sites at the vanadium oxide surface, a Brønsted and a Lewis acid site, are examined in detail.

3.1. Nitrosamide formation near a Brønsted acid site

In the present calculations on nitrosamide formation at a Brønsted acid site^{12, 15, 17, 19} the reaction site is modeled by an OH group including a vanadyl oxygen O(1) of the ideal V₂O₅(010) surface, represented by a V₁₀O₃₁H₁₂H cluster, see Fig. 1a. The optimized reaction path involves, altogether, five different geometric configurations labeled B1 to B5 and shown by balls-and-sticks

models in Fig. 2. Here configurations B1, B2, B3, B5 refer to local equilibrium states while B4^{ts} denotes a transition state. Corresponding relative reaction energies ΔE of the different configurations are presented in Table 1 and Fig. 3.

The first configuration, **B1**, see Fig. 2a, describes the initial state with the two reactants, NO and NH₃ in gas phase, and the Brønsted acid site cluster with one OH group at a vanadyl oxygen site O(1). This starting point serves as the energy zero for relative reaction energies ΔE along the reaction path shown in Fig.3 and listed in Table 1. The first reaction step is the adsorption of ammonia at the Brønsted OH site of the catalyst surface. As discussed in detail elsewhere²⁰, NH₃ approaching the OH surface site adsorbs without a barrier and forms a highly positively charged ammonium species, NH₄⁺ which is quite strongly bound to the surface. The size and the shape of the tetrahedral NH₄ adsorbate lead to equilibrium geometries which involve more than one oxygen site at the surface. Near the vanadyl ridge NH₄ stabilizes with its nitrogen above the center of four O(1) sites. Three of its hydrogen legs point towards the vanadyl oxygen sites with corresponding OH distances of about 2 Å²⁰ while the remaining hydrogen points away from the surface. This, together with NO in gas phase, yields the first intermediate equilibrium state, **B2**, shown in Fig. 2b. The corresponding relative reaction energy is $\Delta E = -1.36$ eV, see Table 1, Fig. 3, which confirms the highly exothermic adsorption of NH₃.

During the next reaction step the NO molecule approaches the adsorbed NH₄ species at the catalyst surface where it binds rather weakly on top of the adsorbate pointing with its nitrogen end towards the surface. This yields the second intermediate equilibrium state, **B3**, shown in Fig. 2c. The NO adsorbate is tilted slightly with respect to the surface normal and the inter-atomic distance between the nitrogen center and the nearest hydrogen center of NH₄ is rather large, $d(\text{N-H}) = 2.16$ Å. This is consistent with weak binding which is reflected by the relative reaction energy ΔE of the B3 state being lower than that of B2 by only 0.15 eV, see Table 1, Fig. 3.

After the B3 state the energetically suggested reaction path is characterized by NO interacting with the NH₄ species to yield the nitrosamide intermediate, NH₂NO, in one activated double-dehydrogenation step. This step is of crucial importance for the reaction near a Brønsted acid site at the V₂O₅(010) surface and we did not identify additional intermediates and/or transition states which would allow energetically more favorable reaction paths. Starting from the B3 geometry one hydrogen of the NH₄ species splits off to form an OH group with a surface vanadyl oxygen O(1). The resulting NH₃ product together with nearby NO rearranges such that the two nitrogen atoms

bind with each other and one of the hydrogen legs of the NH_3 moves towards a nearby surface vanadyl site O(1) to form an N - H - O(1) bridge. This describes the transition state **B4^{ts}**, shown in Fig. 2d, whose reaction energy ΔE is above that of the B3 state by 1.52 eV, see Table 1, Fig. 3, and corresponds to a rather high reaction barrier.

The bond making/breaking process during the endothermic reaction between the intermediate state B3 and the transition state B4^{ts} becomes obvious in an analysis of inter-atomic distances. In the B4^{ts} state the hydrogen split off from NH_4 to approach a vanadyl site O(1) (lower left part of Fig. 2d) yields a distance $d(\text{O}(1)\text{-H}) = 0.98 \text{ \AA}$ which is typical of an isolated OH group at the surface²⁰. Further, the distance between the nitrogen of the NH_3 product and that of the adjacent NO (upper central part of Fig. 2d) amounts to $d(\text{N-N}) = 1.57 \text{ \AA}$ which is only $0.22 \text{ \AA}$ larger than the corresponding N-N bond length calculated for the isolated NH_2NO molecule. This gives clear indications of an interatomic bond being created. Finally, the hydrogen of the N - H - O(1) bridge (lower central part of Fig. 2d), which results from hydrogen moving between nitrogen of the NH_3 species and oxygen at the O(1) site, leads to inter-atomic distances $d(\text{N-H}) = 1.32 \text{ \AA}$ and $d(\text{O}(1)\text{-H}) = 1.19 \text{ \AA}$. This is analogous to the transition state geometry for diffusion of hydrogen between different oxygen sites of the $\text{V}_2\text{O}_5(010)$ surface²¹.

After the transition state B4^{ts} the optimized reaction path leads directly to the nitrosamide species weakly adsorbed at the $\text{V}_2\text{O}_5(010)$ surface, see Fig. 2e, in an exothermic process without a further activation barrier. Starting from the transition state geometry B4^{ts} the N-H bond of the corresponding N - H - O(1) bridge is broken leaving an O(1)H group behind. The resulting NH_2NO group reorients itself such that it points with the nitrogen of the NO part towards one O(1)H group of the catalyst surface and one hydrogen of the NH_2 part towards a neighboring O(1) site. This yields the intermediate equilibrium state **B5** shown in Fig. 2e whose reaction energy ΔE is lower than that of the transition state B4^{ts} by 0.67 eV, see Table 1, Fig. 3. The subsequent decomposition of the NH_2NO into molecular N_2 and H_2O at the $\text{V}_2\text{O}_5(010)$ surface, starting from the intermediate state B5 and completing the SCR reaction, has been examined in earlier theoretical studies^{12, 15}. In these studies a simple reaction path has been identified which will not be considered here.

Previous DFT cluster studies^{12, 15, 17} on the formation of nitrosamide near Brønsted acid sites at the perfect $\text{V}_2\text{O}_5(010)$ surface found, in agreement with the reaction mechanism discussed above, that NO reacting with surface NH_4 can lead to NH_2NO . However, these authors propose an additional stable intermediate species, NH_3NOH ,^{12, 15, 17} beyond the one identified in the present

work. This intermediate arises from the nitrogen of the approaching NO inserting itself between one of the N-H bonds of the surface NH_4 species in an activated process which is accompanied by a reaction barrier of 1.1 eV¹⁷ (starting from a state analogous to B2 and NO in gas phase). However, the NH_3NOH intermediate is stabilized by only -0.02 eV¹⁷ which raises the question whether it represents a truly stable intermediate. The subsequent transition, leading from NH_3NOH to the final intermediate, NH_2NO , is found to be also activated with a reaction barrier of 0.4 eV¹⁷. Thus, the total barrier of the two partial steps combined amounts to 1.5 eV which agrees nicely with the barrier value obtained in the present study ($\Delta E(\text{B4}^{\text{ts}}) - \Delta E(\text{B3}) = 1.52$ eV, see Table 1) where a single transition step is identified.

3.2. Nitrosamide formation near a Lewis acid site

In the following we discuss nitrosamide formation at a Lewis acid site according to an ‘amide-nitrosamide’ type mechanism proposed first by Ramis et al.²². In contrast to previous studies¹⁷ starting from Lewis sites at clean vanadium oxide surfaces, we consider a reduced vanadium atom V_{red} below a surface vanadyl oxygen vacancy site $\text{O}(1)_{\text{vac}}$ as a model of the active Lewis acid site. This can be represented by a $\text{V}_{10}\text{O}_{30}\text{H}_{12}$ cluster, see Fig. 1b. The optimized reaction path is more complex than before and involves, altogether, eleven different geometric configurations labeled L1 to L11 and shown by balls-and-sticks models in Figs. 4-6. Here configurations L3^{ts} , L6^{ts} , L8^{ts} , L10^{ts} , denote transition states while the others refer to local equilibrium states. Corresponding relative reaction energies ΔE of the different configurations are presented in Table 2 and Fig. 7.

The initial configuration, **L1**, see Fig. 4a, of the reaction is described by the two reactants, NO and NH_3 in gas phase, and the Lewis acid site cluster with one vanadyl oxygen $\text{O}(1)$ removed and the vanadium neighbor below serving as the Lewis site. This starting point defines the energy zero for relative reaction energies ΔE along the reaction path shown in Fig. 7 and listed in Table 2. Analogous to the Brønsted scenario of Sec. 3.1, the first reaction step is the adsorption of ammonia but in the Lewis scenario it occurs at a site above the reduced vanadium of the catalyst surface. As discussed earlier²⁰, NH_3 approaching the reduced vanadium site adsorbs without a barrier and is rather strongly bound above the vanadium V_{red} at a N-V distance of 2.09 Å. This, together with NO in gas phase, yields the first intermediate equilibrium state, **L2**, shown in Fig. 4b. The corresponding relative reaction energy is $\Delta E = -1.52$ eV, see Table 2, Fig. 7, which confirms the highly exothermic adsorption of NH_3 , in analogy with the Brønsted scenario.

Following the amide-nitrosamide SCR reaction mechanism, as proposed in Ref. 22 the adsorbed NH_3 splits into adsorbed NH_2 and hydrogen in an activated process before it can react with NO. This dehydrogenation reaction is described by one hydrogen of the adsorbed NH_3 being transferred to a neighboring O(1) oxygen site. In the transition state $\mathbf{L3}^{\text{ts}}$, see Fig. 4c, the hydrogen is already close to the O(1) oxygen forming a local OH group as indicated by the inter-atomic distance, $d(\text{O}(1)\text{-H}) = 0.98 \text{ \AA}$, being characteristic for isolated OH groups at the surface²⁰. At the same time the distance between the nitrogen atom of the remaining NH_2 species and the transferring hydrogen amounts to $d(\text{N-H}) = 2.42 \text{ \AA}$ which indicates a substantial N-H bond weakening. This is accompanied by the remaining NH_2 binding more strongly with the reduced vanadium at the surface which yields a distance $d(\text{V-N}) = 1.86 \text{ \AA}$ for the NH_2 species in the transition state $\mathbf{L3}^{\text{ts}}$, shorter by $0.23 \text{ \AA}$ compared with that of the NH_3 adsorbate in the equilibrium state $\mathbf{L2}$, see Figs. 4b, c. The computed energy barrier for this dehydrogenation step, path $\mathbf{L2}$ to $\mathbf{L3}^{\text{ts}}$, amounts to 0.68 eV as determined by differences of the relative reaction energies, see Table 2 and Fig. 7. This is significantly smaller than the dehydrogenation energy of NH_3 , 1.52 eV , evaluated for the perfect surface²¹. Thus reduction of the surface not only supports the initial adsorption but also facilitates the dehydrogenation of NH_3 . After passing through the transition state the resulting NH_2 adsorbate and the O(1)H group both rotate locally to achieve the intermediate equilibrium configuration $\mathbf{L4}$, see Fig. 4d. The rotation affects the binding energetics only little which is indicated by the relative reaction energy ΔE at $\mathbf{L4}$ being below that of $\mathbf{L3}^{\text{ts}}$ by only 0.08 eV , see Table 2 and Fig. 7.

In the subsequent reaction step the NO molecule from gas phase approaches the adsorbed NH_2 species at the catalyst surface and binds rather weakly, analogous to the Brønsted acid site reaction discussed in Sec. 3.1. In the corresponding intermediate equilibrium configuration $\mathbf{L5}$, see Fig. 5a, the NO molecule points with its nitrogen end towards a hydrogen of the adsorbed NH_2 species. The corresponding inter-atomic distance, $d(\text{N-H}) = 2.39 \text{ \AA}$, is quite large and the adsorption energy, determined by differences of the relative reaction energies, see Table 2 and Fig. 7, is rather small, only -0.12 eV which is consistent with weak binding. The two surface species, NH_2 and NO, react further with each other to form the intermediate NH_2NO in its final configuration where the present calculations show that the minimum energy path involves three steps.

First, the NO molecule interacts simultaneously with the adsorbed NH_2 and the reduced vanadium in an activated process to yield an intermediate equilibrium state $\mathbf{L7}$ where both NO and NH_2 co-adsorb at the reduced vanadium site, see Fig. 5c. The corresponding transition state $\mathbf{L6}^{\text{ts}}$, see Fig. 5b, reflects a reaction barrier of 0.52 eV , see Table 2 and Fig. 7, which is significantly

smaller than the barrier obtained for the reaction near a Brønsted acid site, 1.52 eV, as discussed above, see Table 1. In the transition state **L6^{ts}** the bond between NH_2 and the surface becomes weaker due to the interaction with NO, yielding a distance $d(\text{V-NH}_2) = 2.00 \text{ \AA}$, while the bond length of NO with the surface, $d(\text{V-NO}) = 2.37 \text{ \AA}$, is still large. Here the distance between the nitrogen atoms of the adsorbate complex $d(\text{N-N}) = 1.88 \text{ \AA}$ is still substantially longer than the corresponding distance calculated for gas phase nitrosamide, NH_2NO , $d(\text{N-N}) = 1.35 \text{ \AA}$. In the intermediate state **L7** the bond between NO and the surface is strengthened further while NH_2 moves away from the vanadium site. This is characterized by distances $d(\text{V-NO}) = 1.85 \text{ \AA}$, $d(\text{V-NH}_2) = 2.14 \text{ \AA}$, and an inter-atomic nitrogen distance of the adsorbate complex shortened to $d(\text{N-N}) = 1.47 \text{ \AA}$ indicating formation of a surface nitrosamide species. As a result, the intermediate state **L7** is energetically lower than **L6^{ts}** by 0.40 eV as determined by differences of the relative reaction energies, see Table 2 and Fig. 7.

Second, starting from configuration **L7** the NO molecule pushes with its nitrogen end between the vanadium atom and the adsorbed NH_2 adsorbate in an activated process which increases the distance further, to $d(\text{V-NH}_2) = 2.57 \text{ \AA}$ in the transition state **L8^{ts}** and to $d(\text{V-NH}_2) = 2.95 \text{ \AA}$ in the following intermediate equilibrium state **L9**, see Figs. 5d, e. The corresponding energy barrier amounts to only 0.13 eV while the intermediate state **L9** is 0.44 eV below the transition state **L8^{ts}**, see Table 2, and, thus, rather stable. The resulting NH_2NO complex in the **L9** state is bound mainly by its nitrogen from the NO part with the reduced surface vanadium at a bond length of $d(\text{V-NONH}_2) = 1.96 \text{ \AA}$, see Fig. 6e. The respective nitrogen-nitrogen distance, $d(\text{N-N}) = 1.40 \text{ \AA}$, is larger by only 0.05 $\text{\AA}$ compared with that calculated for gas phase nitrosamide.

Third, the nitrosamide of the intermediate state **L9** is not yet positioned in a geometry which allows easy decomposition to gas phase N_2 and H_2O as discussed in previous theoretical studies^{12, 15}. This geometry, described by NH_2NO binding simultaneously with an $\text{O}(1)\text{H}$ group and an adjacent $\text{O}(1)$ oxygen at the vanadium oxide surface, can be reached from state **L9** in an additional activated diffusion process. Here the V-NO bond of the **L9** state is broken and the NH_2NO moves towards the neighboring $\text{O}(1)\text{H}$ group at the surface where the oxygen of the NO part couples with $\text{O}(1)\text{H}$ and one of the hydrogen atoms of the NH_2 part binds with the adjacent $\text{O}(1)$, see Fig. 6b for the transition state **L10^{ts}** and Fig. 6c for the intermediate equilibrium configuration **L11**. The energy barrier for this diffusion step is 0.86 eV while the intermediate configuration **L11** is energetically below **L10^{ts}** by only 0.05 eV, see Table 2 and Fig. 7.

The comparison of NH_2NO formation near the Lewis acid (reduced vanadium) site at the $\text{V}_2\text{O}_5(010)$ surface with that near a Brønsted acid site (surface OH group) shows significant differences between the two reaction paths. First, the number of reaction steps for the Lewis site, six, is larger than the three steps for the Brønsted site. Second, the largest individual barrier for the Lewis site, the final diffusion barrier with a height of $\Delta E(\text{L10}^{\text{ts}}) - \Delta E(\text{L11}) = 0.86 \text{ eV}$, is significantly lower than the (only) barrier describing the final NH_2NO formation step where a height of $\Delta E(\text{B4}^{\text{ts}}) - \Delta E(\text{B3}) = 1.52 \text{ eV}$ is obtained. Altogether, these findings suggest that Lewis acid sites of the reduced surface, supporting an amide-nitrosamide type of mechanism²² may become important for possible reaction scenarios describing the SCR process.

As discussed in the first paper of our series²⁰, the adsorption of NO and NH_3 at reduced vanadium sites is energetically very similar. The adsorption energies for both relevant sites (near vacancies $\text{O}(1)_{\text{vac}}$ and $\text{O}(1')_{\text{vac}}$, respectively) differ by less than 0.15 eV with $E_{\text{ads}}(\text{NO})$ being slightly larger than $E_{\text{ads}}(\text{NH}_3)$. This could suggest adsorption of NO before NH_3 stabilizes at the surface. However, it should be emphasized that the present SCR mechanism involves decomposition of NH_3 to $\text{NH}_2 + \text{H}$ at the substrate surface where the reaction barrier is much lower without than with pre-adsorbed NO.

So far, only one theoretical study examined possible reaction paths on the formation of nitrosamide near a Lewis acid site of the $\text{V}_2\text{O}_5(010)$ surface applying DFT methods using a GGA-hybrid functional¹⁷. However, in this study the reaction site was modeled by a vanadium center of the perfect surface in contrast to the present work where vanadium of the reduced surface is considered. In agreement with our previous theoretical studies^{20, 21} it was found that ammonia interacts quite weakly with the perfect $\text{V}_2\text{O}_5(010)$ surface and, in addition, the dehydrogenation of weakly adsorbed NH_3 to yield NH_2 is highly endothermic¹⁷. The latter makes the resulting SCR reaction path energetically unfavorable compared with the reaction near a Brønsted acid site of the perfect $\text{V}_2\text{O}_5(010)$ surface. This may explain why other theoretical studies^{12, 15, 17, 19} excluded reaction mechanisms near Lewis acid sites of the perfect $\text{V}_2\text{O}_5(010)$ surface. However, the present work shows that reaction mechanisms near Lewis acid sites of the reduced $\text{V}_2\text{O}_5(010)$ surface need to be considered in a complete description of the SCR process.

4. CONCLUSION

The present cluster model studies build on our previous work on adsorption properties, geometric, energetic, and electronic quantities, as well as diffusion and reaction of different adsorbate species that can occur at a vanadium oxide surface where the selective catalytic reduction (SCR) of NO in the presence of ammonia proceeds^{20, 21, 28}. Extended cluster models together with density-functional theory (DFT) are used to examine optimized reaction paths of the SCR where we consider two different reaction scenarios of the SCR suggested by our earlier work^{20, 21}. First, we examine the SCR near Brønsted acid sites of the perfect vanadium oxide surface, which are modeled by OH groups at a single crystal $V_2O_5(010)$ surface. Second, we consider the SCR for the first time near Lewis acid sites of the *reduced* surface, where reduction is modeled by surface oxygen vacancies at single crystal $V_2O_5(010)$ substrate. Previous theoretical studies on SCR scenarios at vanadium oxide substrate suggest that the reaction intermediate nitrosamide, NH_2NO , formed at the substrate surface can decompose to molecular N_2 and H_2O quite easily, i.e. with small energy barriers^{12, 15}. Therefore, this decomposition is not considered in the present work and the study focuses on catalytic reaction steps starting from gas phase NO and NH_3 resulting in the NH_2NO intermediate.

The optimized path of the first reaction scenario near a Brønsted acid site involves three different steps starting with NH_3 adsorbing at a surface OH group which leads to surface NH_4 . Then the NO molecule binds quite weakly with its nitrogen end on top of the NH_4 adsorbate. The resulting NH_4NO intermediate can then rearrange and react at the surface to yield in one activated double-dehydrogenation step the nitrosamide intermediate, NH_2NO which is weakly adsorbed at the oxide surface. The energy ΔE of the corresponding activation barrier obtained by the present calculations is rather high amounting to 1.52 eV and determines the rate limiting step. The optimized path of the second reaction scenario near a Lewis acid site, involving six different steps, starts with NH_3 adsorbing at a reduced vanadium atom which leads to a VNH_3 surface group. Then the NH_3 adsorbate splits in an activated process with a barrier $\Delta E = 0.68$ eV into surface NH_2 and hydrogen where the latter leads to an adjacent surface OH group. In the next step the NO molecule binds rather weakly with the NH_2 adsorbate forming a precursor NH_2NO group. Subsequently, this NH_2NO species rearranges and reacts at the surface to yield the nitrosamide intermediate in its final configuration in three activated reaction steps with barriers $\Delta E = 0.52$ eV, 0.13 eV, and 0.86 eV, respectively, where the latest determines the rate limiting step.

The comparison of NH_2NO formation near Brønsted acid sites of the perfect vanadium oxide surface with that near Lewis acid sites of the reduced surface evidences major differences. First, the number of reaction steps, three for the Brønsted site mechanism vs. six for the Lewis site mechanism, differ. Second, details of the reaction intermediates, NH_4 double-dehydrogenation (Brønsted mechanism) vs. NH_3 dehydrogenation (Lewis mechanism), differ. Third, the largest individual activation barriers determining the reaction rates, $\Delta E(\text{B4}^{\text{ts}}) - \Delta E(\text{B3}) = 1.52 \text{ eV}$ (Brønsted mechanism) vs. $\Delta E(\text{L10}^{\text{ts}}) - \Delta E(\text{L11}) = 0.86 \text{ eV}$ (Lewis mechanism), differ. However, the two mechanisms do not exclude each other and are very likely to occur simultaneously in experiments at real vanadium oxide catalysts. Altogether, these findings suggest that Lewis acid sites of the reduced surface, studied here for the first time, can support an amide-nitrosamide type mechanism²². The theoretical results of this work are consistent with experimental findings and emphasize the importance of surface reduction for the SCR process. They can serve as a basis to describe model reaction paths leading to a more detailed understanding of the SCR process on a microscopic scale.

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Tables

Table 1. Relative reaction energies, ΔE , of intermediate equilibrium and transition states along the calculated reaction paths for nitrosamide formation near a Brønsted acid site (O(1)H group). The energy zero refers to the sum of total energies of the substrate cluster $V_{10}O_{31}H_{12}$ and NH_3 , NO in gas phase. The states are labeled B1, ... B5 with superscript “ts” denoting transition states, see also Fig. 2.

States	B1	B2	B3	B4 ^{ts}	B5
ΔE [eV]	0.00	-1.36	-1.51	0.01	-0.66

Table 2. Relative reaction energies, ΔE , of intermediate equilibrium and transition states along the calculated reaction paths for nitrosamide formation near a Lewis acid site (vanadium neighbor of O(1) vacancy). The energy zero refers to the sum of total energies of the vacancy cluster $V_{10}O_{30}H_{12}$ and NH_3 , NO in gas phase. The states are labeled L1, ... L11 with superscript “ts” denoting transition states, see also Fig. 7.

States	L1	L2	L3 ^{ts}	L4	L5	L6 ^{ts}
ΔE [eV]	0.00	-1.52	-0.84	-0.92	-1.04	-0.52

States	L7	L8 ^{ts}	L9	L10 ^{ts}	L11
ΔE [eV]	-0.92	-0.79	-1.23	-0.37	-0.42

FIGURE CAPTIONS

- Fig. 1. Cluster models used to represent sections of the catalyst surface near Brønsted and reduced Lewis acid sites: (a) Brønsted acid site cluster $V_{10}O_{31}H_{12}H$, (b) Lewis acid site cluster $V_{10}O_{30}H_{12}$. Vanadium atoms are shown by large yellow balls, oxygen by red balls, active hydrogen atoms by small blue, and terminal hydrogen by small gray balls. The active, Brønsted acid (Fig. 1a), and Lewis acid sites (Fig. 1b) are emphasized by hatching.
- Fig. 2. Balls-and-sticks models of geometric configurations computed for initial, intermediate, and final states (a) B1, (b) B2, (c) B3, (d) B4^{ts}, (e) B5 along the reaction path of nitrosamide formation at a Brønsted acid site of the $V_2O_5(010)$ surface, see text. Vanadium atoms are shown by large yellow, oxygen atoms by red balls, nitrogen atoms by green, active hydrogen atoms by small blue, and saturation hydrogen by small light gray balls. Molecules positioned inside the upper right boxes of the figures refer to gas phase species.
- Fig. 3. Relative reaction energies, ΔE , of initial, intermediate, and final states B1 – B5 along the reaction path of nitrosamide formation at a Brønsted acid site of the $V_2O_5(010)$ surface, see Table 1 and text. Local equilibrium states are shown by full dots while transition states are indicated by white circles. All energies are given in [eV]
- Fig. 4. Balls-and-sticks models of geometric configurations computed for initial and intermediate states (a) L1, (b) L2, (c) L3^{ts}, (d) L4 along the reaction path of nitrosamide formation at a Lewis acid site of the $V_2O_5(010)$ surface, see text. Vanadium atoms are shown by large yellow, oxygen atoms by red balls, nitrogen atoms by green, active hydrogen atoms by small blue, and saturation hydrogen by small light gray balls. Molecules positioned inside the upper right boxes of the figures refer to gas phase species.
- Fig. 5. Balls-and-sticks models of geometric configurations computed for intermediate states (a) L5, (b) L6^{ts}, (c) L7, (d) L8^{ts}, (e) L9 along the reaction path of nitrosamide formation at a Lewis acid site of the $V_2O_5(010)$ surface, see text and caption of Fig. 4.
- Fig. 6. Balls-and-sticks models of geometric configurations computed for intermediate and final states (a) L9, (b) L10^{ts}, (c) L11 along the reaction path of nitrosamide formation at a Lewis acid site of the $V_2O_5(010)$ surface, see text and caption of Fig. 4.

Fig. 7. Relative reaction energies, ΔE , of initial, intermediate, and final states L1 – L11 along the reaction path of nitrosamide formation at a Lewis acid site of the $V_2O_5(010)$ surface, see Table 2 and text. Local equilibrium states are shown by full dots while transition states are indicated by white circles. All energies are given in [eV]