Ammonium adsorption on Brønsted acidic centers on low-index vanadium pentoxide surfaces

Maciej Szaleniec · Agnieszka Drzewiecka-Matuszek · Małgorzata Witko · Paweł Hejduk

Abstract Vanadium-based catalysts are used in many technological processes, among which the removal of nitrogen oxides (NOx) from waste gases is one of the most important. The chemical reaction responsible for this selective catalytic reaction (SCR) is based on the reduction of NOx molecules to N2, and a possible reductant in this case is pre-adsorbed NH3. In this paper, NH3 adsorption on Brønsted OH acid centers on low-index surfaces of V2O5 (010, 100, 001) is studied using a theoretical DFT method with a gradient-corrected functional (RPBE) in the embedded cluster approximation model. The results of the calculations show that ammonia molecules are spontaneously stabilized on all low-index surfaces of the investigated catalyst, with adsorption energies ranging from −0.34 to −2 eV. Two different mechanisms of ammonia adsorption occur: the predominant mechanism involves the transfer of a proton from a surface OH group and the stabilization of ammonia as an NH4+ cation bonded to surface O atom(s), while an alternative mechanism involves the hydrogen bonding of NH3 to a surface OH moiety. The latter binding mode is present only in cases of stabilization over a doubly coordinated O(2) center at a (100) surface. The results of the calculations indicate that a nondirectional local electrostatic interaction with ammonia approaching a surface predetermines the mode of stabilization, whereas hydrogen-bonding interactions are the main force stabilizing the adsorbed ammonia. Utilizing the geometric features of the hydrogen bonds, the overall strength of these interactions was quantified and qualitatively correlated (R=0.93) with the magnitude of the stabilization effect (i.e., the adsorption energy).

Keywords SCR · NOx removal · V2O5 · NH3 adsorption · DFT calculations

Introduction

V2O5-based catalysts are of great importance in the catalytic reactions used to care for and protect the environment, such as de-NOx processes. These reactions are mainly responsible for the removal of the waste gases that are the products of liquid or gaseous fuel combustion [1]. The interest in using vanadium-based catalysts in industry is also a result of their resistance to SO2 poisoning. One useful process is the selective catalytic reduction (SCR) of nitrogen oxides (NOx) in the presence of ammonia, which can proceed either in the absence or in the presence of oxygen. Both processes are called “standard SCR” [2–20] and proceed according to the following equations:

\[ \text{6 NO} + 4\text{NH}_3 \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \]

\[ \text{4NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}. \]

In 2002, the reaction mechanism of so-called fast SCR was proposed by Koebel et al. [21, 22] and by Madia et al.: [23]:

\[ \text{2NO} + 2\text{NO}_2 + 4\text{NH}_3 = 4\text{N}_2 + 6\text{H}_2\text{O}. \]

In the fast SCR process, the catalyst is re-oxidized by nitrogen dioxide instead of by the oxygen molecule, and the rate of this reaction is ten times higher than that for the standard SCR process. However, such acceleration occurs only for the equimolecular NO and NO2 mixture, and the reaction rate decreases dramatically if the fraction of NO2 is
larger than 50%. In all SCR processes, side reactions such as NH₃ oxidation to NO, NO₂, or N₂O (competition with SCR at high temperature) or the formation of ammonium nitrate (catalyst poisoning) occur.

The mechanism of the standard SCR reaction, in which nitrogen oxide is reduced to pure nitrogen and water, is still not fully clear; therefore, this mechanism has been investigated extensively by both experimentalists and theoreticians. Many attempts to understand this process have been made in the last few years, and two mechanisms are postulated, namely the Eley–Rideal and Langmuir–Hinshelwood mechanisms. According to the Eley–Rideal mechanism [24–42], ammonia is adsorbed and activated at Bronsted centers. Next, an NH₃ species reacts with the gas-phase or weakly adsorbed NO molecule to yield a dinitrogen molecule and water, whereas the reduced surface (i.e., V–OH groups) is re-oxidized to V=O by O₂ from the gas phase or O from the bulk. The Langmuir–Hinshelwood mechanism [43–46] also postulates ammonia adsorption. However, NO is first oxidized by gaseous O₂ to NO₂, and then the reaction between the adsorbed ammonia and the adsorbed NO₂ species occurs. The reduced Bronsted centers are regenerated by a water molecule. Although these two mechanisms agree with the results of an experiment suggested by Topsøe et al. [2, 5], the SCR reaction proceeds according to both the Eley–Rideal and the Langmuir–Hinshelwood mechanisms. This conclusion is supported by the fact that NO molecules can be adsorbed at the coordinatively unsaturated metallic centers at the catalyst surface, thus reacting easily as weakly adsorbed species.

The main discussion in the literature concerns the forms of both the NH₃ and NO molecules. Table 1 lists the postulated active forms of both substrates in the SCR reaction for different catalysts. In the case of the reactions catalyzed by pure V₂O₅, the NH₃ molecule is adsorbed at the Bronsted acid centers in the form of NH₄⁺ cations, whereas NO is in the gaseous phase; the reaction occurs via the Eley–Rideal mechanism. However, the detailed mechanism of the simple activation of the ammonia molecule is still a matter of controversy, especially regarding the localization of the active sites responsible for this elementary step. Miyamoto and Inomata et al. [24–27] suggested that the active Bronsted centers are localized at the (010) surface of V₂O₅, whereas Gasior and Haber [42] indicated planes that host the surface OH groups. The existence of Bronsted acid sites at the unsaturated (001) and (100) faces of the V₂O₅ crystals was also confirmed by Andersson [51], who postulated that these net planes are responsible for the adsorption and dissociation of a water molecule, which consequently leads to surface hydroxylation. Moreover, Ozkan et al. [39–41] also demonstrated that the hypocoordinated (001) and (100) net planes of V₂O₅ serve as active faces in the SCR mechanism, and the (010) face is mainly responsible for the ammonia oxidation reactions. It has also been suggested that ammonia can be coordinatively adsorbed on the surface vanadium cations, which act as the Lewis acidic centers in the form of V–NH₃ or V–NH₂ species.

In this study, the first step in the selective catalytic reduction of NOx by ammonia is discussed, mainly involving NH₃ adsorption on the surface OH groups (Bronsted acid centers) that are present at three low-index V₂O₅ surfaces. There have been a number of theoretical studies of the ammonia adsorption on Bronsted acid sites using both cluster [26, 49, 50, 52–58] and periodic [59, 60] approaches at different levels of theory, including the semiempirical level [26], post-Hartree methods [61], and the density functional theory level [49, 50, 52, 53, 55–61]. The conclusions from these investigations are similar and indicate that, in almost all cases, ammonia is stabilized at surface OH groups in the form of NH₄⁺ cations, as postulated on the basis of experimental results. However, the above studies are focused only on the (010) V₂O₅ net plane, but it is known that vanadium crystals can expose other low-index surfaces, such as coordinatively unsaturated (100) and (001) surfaces. The fact that approximately 15% of the overall contribution to the crystallite structure comes from these surfaces [62] indicates that unsaturated surfaces might play an important role in the catalytic process, as was postulated by Haber [42] and Ozkan [39–41]. The present paper discusses ammonia adsorption on OH centers of all three low-index V₂O₅ surfaces. Two different modes of ammonia stabilization are reported: (i) an NH₄⁺ moiety hydrogen bonded to surface oxygen atoms and (ii) an NH₂ moiety hydrogen bonded to the surface OH group. The mode and strength of the ammonia stabilization over various adsorption sites are discussed in terms of the local electrostatic potential of the surface binding sites and the strength of the hydrogen bonds.

| Active form of: | Catalyst | Postulated active center(s) | Reference(s) |
|----------------|----------|-----------------------------|--------------|
| NH₃⁺ NO₂ (ads) | V₂O₅    | V=O, V–OH                  | [43–45]      |
| NH₃⁺ NO (gas)  | V₂O₅    | V=O, V–OH                  | [24–27]      |
| NH₃⁺ NO (gas)  | V₂O₅    | V=O, V–OH                  | [42]         |
| NH₃⁺ NO (ads)  | V₂O₅/TiO₂ | V=O, V–OH                 | [4, 47]      |
| NH₃⁺ NO (gas)  | V₂O₅    | V=O, V–OH                  | [39–41]      |
| NH₃⁺ NO (gas)  | V₂O₅/TiO₂ | V=O, V–OH                  | [39–41]      |
| NH₃⁺ NO (ads)  | V₂O₅/TiO₂ | V=O, V–OH                  | [39–41]      |
| V–O–NH₃ NO (gas) | V₂O₅/support | V=O, V–OH                  | [35, 36]      |
| V–NH₂ NO (gas) | V₂O₅/TiO₂ | V=O                        | [48]         |
| NH₃(ads) NO (gas) | V₂O₅/support | Lewis acid centers        | [46]         |
| NH₂ NO (ads)   | V₂O₅/TiO₂ | V=O                        | [49]         |
| NH₄⁺ NO (ads)  | V₂O₅/WO₄ | V=O/W=O                    | [50]         |

Reference(s): [42, 43–45, 46, 47–52, 54–58, 59, 60, 61, 62]
formed between the ammonia molecule and the surface oxygen atoms.

**Models and computational details**

**Model setup**

The crystal lattice of vanadium pentoxide has an orthorhombic symmetry and is assigned to the space group $D_{2h}^1-Pmn2_1$, with unit cell parameters defined as $a=11.51$ Å, $b=4.37$ Å, $c=3.56$ Å [63, 64]. The building unit forms a distorted octahedron with V–O bond distances varying between very short (1.58 Å, vanadyl groups) and very long (2.79 Å, van der Waals type bonding). Three possible low-index surfaces exist: the saturated (010) and unsaturated (001 and 100) surfaces are shown in Fig. 1.

The most thermodynamically stable (010) surface [62] (Fig. 1a) is characterized by three structurally different oxygen sites: (i) terminal vanadyl oxygen atoms O(1), which are singly coordinated to vanadium atoms and protrude from the surface in rows, and two bridging oxygen sites that are (ii) doubly, i.e., O(2), or (iii) triply, i.e., O(3), coordinated to vanadium centers. The unsaturated (001) surface (Fig. 1b), which is described by the existence of “valley”- and “hill”-like regions, exhibits coordinatively unsaturated vanadium atoms and three structurally different oxygen sites that lie in the plane (Fig. 1b): vanadyl oxygen O(1) and bridging O(2) or $O^\ddagger(2)$ oxygen atoms coordinated to two vanadium atoms (the $O^\ddagger(2)$ atom is connected to two vanadium atoms from different atomic layers and positioned on the surface edges). The unsaturated (100) surface may have a different termination [62]; the most thermodynamically stable structure is shown in Fig. 1c and contains unsaturated V centers and in-plane singly (O(1)) and doubly (O(2)) coordinated sites.

The $V_{10}O_{31}H_{12}$ cluster (Fig. 2) was selected as a model of the (010) surface, as described in our previous studies [65], in order to discuss electronic/adsorption properties of the (010) net plane. To mimic the (001) $V_2O_5$ surface, the $V_{21}O_{65}H_{25}$ cluster was used to describe both the “hill” and “valley” regions (Fig. 2). The $V_{10}O_{52}H_{24}$ cluster (Fig. 2) was chosen as the most appropriate model to characterize the (100) $V_2O_5$ net plane [65]. For all clusters, the dangling bonds of the peripheral O atoms were saturated with H atoms, forming OH groups and neutralizing the clusters [66, 67]. All initial clusters selected as surface models were closed shell. To prepare sites for ammonia adsorption, an additional H atom was added to the selected surface oxygen sites, thus forming surface OH groups and leading to the doublet systems [56, 68]. This procedure simulated the mechanism of surface OH formation under the reaction conditions (e.g., by dissociative adsorption of $H_2O$ [69] or the reaction of $NH_3$ and NO on the $V^{5+}=O$ sites [70]).

**Calculation procedure**

The program StoBe, the local version of DeMon, was applied to perform the calculations [71]. This used an ab initio density functional theory (DFT) method in which the Kohn–Sham orbitals were represented by a linear combination of atomic orbitals (LCAOs). For constrained geometry optimization of all cluster models, we applied the revised version of the gradient corrected functional of Perdew–Burke–Ernzerhof (RPBE) [72, 73] with all-electron DZVP basis sets of contracted Gaussians [74, 75]. This functional proved suitable for studying the interactions of small molecules with a broad range of adsorption sites, ranging from metal oxides to transition metal complexes [69, 76–81]. Models were subjected to partial geometry optimization using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm according to the procedure described in [65]. In short, only the local environment near to each oxygen adsorption site was allowed to relax for both H and $NH_3$ absorption. The local environment of a particular oxygen was defined by its nearest V neighbors together with the oxygen atoms linked to these metal atoms and the adsorbate molecule. The rest of the atoms were kept frozen at their crystallographic positions. The vibration analysis for the final $V_2O_3–H–NH_3$ complexes was performed only for the geometry-relaxed sections, and no imaginary frequencies indicating local energy minima were observed.
The structure of the model with an OH group was obtained by adding the hydrogen atom to a particular oxygen site and then performing geometry relaxation, as described in [82]. Hydrogen becomes stabilized at all oxygen sites present on three low-index V2O5 surfaces, with this process being spontaneous, as shown by periodic calculations [83]. The figures presenting the structures of clusters with adsorbed hydrogen atoms are provided in the “Electronic supplementary material” (ESM; Figs. S1–S3).

A detailed analysis of the electronic structure of each cluster was performed using the charge density distribution (Mulliken populations) [84], the Mayer bond orders [85, 86], and an analysis of electrostatic potentials. The electrostatic potentials were calculated 2 Å above each adsorbed hydrogen atom (i.e., x, y coordinates of the hydrogen atom). Such an approach provided a uniform and objective method for estimating the electrostatic interaction of the local surface with an NH3 molecule before a hydrogen bond is formed, which can result in the potential transfer of the H+ from the surface OH to the adsorbate. On the other hand, in order to estimate the electrostatic interaction of the surface with the already adsorbed NH4+/NH3 moiety, the electrostatic potential was calculated for the respective surface (i.e., “bare” or with an OH group) at the coordinates of the N atom of the adsorbate.

The ammonia adsorption energies were calculated according to the following equation:

\[
E_{\text{ads}} = E_{\text{tot}}(\text{cluster} + \text{NH}_3) - [E_{\text{tot}}(\text{cluster}) - E_{\text{tot}}(\text{NH}_3)],
\]

where \(E_{\text{tot}}(\text{cluster})\) denotes a cluster with a Brønsted acid OH group.

These adsorption energies were corrected for London dispersion forces that are not included in RPBE with the DFT+D2 procedure using empirical damped dispersion correction [87]. A global scaling factor of 1.25 (s6) was used for RPBE calculations and 0.75 for geometries optimized with the PBE functional [81, 88].

Model validation

The influence of the basis set on the adsorption energies calculated with the RPBE functional was investigated by performing RPBE/TZVP single point calculations for the (010) net plane.

In order to cross-validate the performance of the RPBE functional, we conducted test calculations for NH3 adsorption on O sites of the (010) net plane in Turbomole v.6.3 [89] with the gradient-corrected Perdew–Burke–Ernzerhof (PBE) functional [90–93] and the def-TZVP all-electron basis set [94]. The resolution of identity (RI) approach was applied to compute the electronic Coulomb interactions [95, 96]. Complete geometry optimization was performed for the (010) models with the exception of terminal oxygen atoms terminated with hydrogen atoms. The positions of terminal O and H atoms were frozen in order to preserve the structural constraints imposed by the surface structure. The locations of energetic minima were confirmed by vibration analysis and by checking for a lack of imaginary frequencies. The structures of the respective models with adsorbed hydrogen and ammonium ion are presented in the ESM (Figs. S4 and S6).

Similar optimizations of unsaturated (001) and (100) model surfaces were not possible, as they led to significant surface reconstruction and yielded an artificial geometry for the V2O5 surface. Comparison of the obtained reconstructed surface structures with model net planes obtained with periodic calculations [83, 97] showed that the partially constrained cluster models described the surface more accurately than the relaxed models in which boundary constraints were imposed. The reconstructed geometries obtained for the (001) and (100) net planes are provided in the ESM.
Results and discussion

The ammonia is stabilized via O–H–N hydrogen bonds with surface hydroxyl groups present at each low-index V$_2$O$_5$ surface. However, the adsorption mechanism and adsorption geometry depend on both the type of center and the type of net plane involved (see Tables 2, S2, and 5).

Table 2 summarizes the data obtained for the process of ammonia adsorption at the three discussed low-index V$_2$O$_5$ surfaces. It contains the adsorption energies ($E_{\text{ads}}(\text{NH}_3)$) and Mulliken atomic charges ($Q$), while Table S2 in the ESM contains the Mayer bond orders (BO) and the distances ($R$) and angles ($\alpha$) of the N···H···O hydrogen bonds.

NH$_3$ adsorption at a (010) V$_2$O$_5$ surface

At the (010) V$_2$O$_5$ surface, ammonia is adsorbed as an NH$_4^+$ cation and stabilized by single or double hydrogen bonds (see Fig. 3 and Figure S4 of the ESM). In all of the studied cases, ammonia is spontaneously adsorbed at each of the adsorption sites (Table 2). The adsorption energies $E_{\text{ads}}(\text{NH}_3)$ attain negative values: $-0.98$ eV, $-1.07$ eV, and $-1.31$ eV ($-30.2$, $-22.6$, and $-24.7$ kcal/mol$^{-1}$, respectively) for stabilization at the O(2), O(3)–O(2), and O(1)–O(1) centers, respectively. The largest adsorption energy ($-1.31$ eV) is observed for the stabilization of two O(1) oxygen sites. The introduction of corrections for London dispersion forces does not change the qualitative description of the adsorption.

The ammonia is stabilized via O(1), O(2), O(3)–O(2), and O(1)–O(1) hydrogen bonds. The introduction of corrections for London dispersion forces lowers the adsorption energy of each site by 0.13 eV ($3.1–7.8$ kcal/mol$^{-1}$). The dispersion attraction appears to be higher for an ammonia ion adsorbed in between double rows of V=O ligands (around 0.3 eV), i.e., for O(2) and O(3), O(2) sites, than for an ammonia ion adsorbed on two O(1) oxygen atoms (0.13 eV). As a result, all three adsorption sites exhibit similar ammonia adsorption energies of 1.32–1.44 eV, although the overall preference for the O(1) site is still maintained. These calculations indicate that, in the case of ammonia ions adsorbed

| Adsorption site | (010) surface | (100) surface | (001) surface | Valley |
|----------------|--------------|--------------|--------------|-------|
|                | O(1), O(1)   | O(2), O(3), O(2) | O(1), O(2), O(2) | O(2), O(1)–O(1) |
| $E_{\text{ads}}$ DZVP (eV) | $-1.31$ | $-0.98$ | $-1.07$ | $-0.86$ | $-0.70$ | $-0.49$ | $-1.97$ |
| $E_{\text{ads}}^{\text{D2H+D2}}$ (eV) | $-1.44$ | $-1.32$ | $-1.40$ | $-1.07$ | $-1.03$ | $-0.72$ | $-2.29$ |
| Mulliken population: | | | | | | | |
| $Q$(NH$_3$) | $+0.48$ | $+0.45$ | $+0.47$ | $+0.41$ | $+0.48$ | $+0.14$ | $+0.60$ |
| $Q$(NH$_4^+$) | $+0.81$ | $+0.87$ | $+0.87$ | $+0.82$ | $+0.83$ | $+0.58$ | $+0.87$ |
on O(2) and (O3) sites, dispersion accounts for ~25% of the stabilization, while dispersion accounts only for 10% of the stabilization of ions adsorbed on the tops of O(1) rows. The above results demonstrate that, at the (010) surface, ammonia is activated according to the same mechanism at Brønsted acid centers. NH$_4^+$ cations act as proton-donating groups in the hydrogen bonds. The formation of hydrogen bonds plays a vital role in ammonia stabilization. Our results are consistent with the recent DFT calculations of Sun et al. [50] and Yuan et al. [49], which showed energetically favorable stabilization of NH$_4^+$ cations by two hydrogen-bonding interactions with O(1) atoms. However, because the clusters used in those studies were very small (V$_2$O$_9$H$_8$ and V$_6$O$_{20}$H$_{11}$, respectively), the authors could not study adsorption at the O(2) or O(3) sites.

NH$_3$ adsorption at the (100) V$_2$O$_5$ surface

At the (100) surface, NH$_3$ is stabilized at the surface hydroxyl groups O(1)H and O(2)H (Fig. 4). In analogy to the (010) V$_2$O$_5$ surface, ammonia undergoes spontaneous adsorption with $E^{ad}(\text{NH}_3)$ values of $-0.86$ and $-0.70$ eV ($-19.8$ and $-16.1$ kcal/mol$^{-1}$) for stabilization at the O(1) and O(2) centers, respectively, while the dispersion-corrected adsorption energies are $-1.07$ and $-1.03$ eV ($-24.6$ and $-23.8$ kcal/mol$^{-1}$) for stabilization at the O(1) and O(2) centers, respectively.

Adsorption at Brønsted acidic vanadyl sites (V–O(1)H) leads to the creation of a single hydrogen bond with a hydrogen donor–acceptor distance (O(1)···N) of 2.54 Å and an NHO bond angle of 179°. At the second adsorption center localized above the surface O(2)H site, ammonia is stabilized by two hydrogen bonds formed between two bridging O(2) oxygen atoms. One strong hydrogen bond is formed between O(2) and an ammonium cation with an O(2)···N distance of 2.67 Å and an NHO angle of 175°, and the other—weak—hydrogen bond is formed with O(2) from a parallel atomic row and has an O(2)···N distance of 2.95 Å and an NHO angle of 178°.

The mechanism of stabilization is similar for both sites, namely the protons shift from the O sites to the ammonia molecule and the formation of NH$_4^+$ is observed.

The cationic form is substantiated by the Mulliken population and a geometry analysis. The total charge on the NH$_4^+$ species is +0.82 for O(1) and +0.83 for the O(2) site.
In the hydrogen bond formed at O(1), the N–H distance is fairly long (d(N–H)=1.17 Å, BO=0.56), whereas the interaction between the hydrogen and oxygen occurs at a short distance and is strongly covalent (d(H–O) 1.38 Å, BO=0.29).

In the case of the O(2) site, the stronger hydrogen bond is characterized by an N–H distance of 1.11 Å (BO=0.70) and an H–O distance of 1.56 Å (BO=0.20). The weaker hydrogen bond has a shorter N–H distance (1.05 Å, BO=0.82) and a longer H–O distance (d(H–O) 1.90 Å, BO=0.08). The stronger H-bonding at O(2) results in closer contact of the ammonium ion with the V2O5 surface than in the case of the O(1) binding site. As a result, the dispersion forces contribute more to stabilizing the adsorption, lowering the overall energy by −0.33 eV (−7.7 kcal/mol) for the O(2) binding site, as compared to −0.21 eV (−4.8 kcal/mol) for the O(1) site.

NH3 adsorption at the (001) V2O5 surface

At unsaturated (001) V2O5 surfaces, the net plane process of ammonia adsorption is more complex because NH3 is stabilized by single and triple hydrogen-bonding interactions that can also be trifurcated toward different donors. As was the case for the two other low-index faces of V2O5, the $E_{\text{ads}}$(NH3) energies indicate that the adsorption of ammonia on Brønsted acid centers at the (001) surface is spontaneous. The adsorption energies $E_{\text{ads}}$(NH3) (Table 2) are −0.49 eV (−11.3 kcal/mol) and −1.97 eV (−45.4 kcal/mol) for the ammonia stabilization at the "hill"-like O(2) and the valley-like O(2), O(2),O(2)–O(1)–O(1) oxygen sites. The dispersion correction lowers the adsorption energy by −0.21 and −0.31 eV (−5.2 and −7.3 kcal/mol) for the hill and the valley regions, respectively. The London attraction force for the hill-like O(2) site is comparable with the dispersion stabilization observed for the (100) O(1) site and twice as big as that calculated for O(1),O(1) sites on the (010) net plane. Interestingly, for valley-like adsorption sites, where ammonia ions seem to have the highest degree of van der Waals contact, the overall stabilization is only −0.32 eV, which is in the range of dispersion stabilization observed for O(2) sites on the (010) or O(2),O(2) sites on the (100) net plane.

Tables 2 and 5 list the stabilization energies and characteristics of the hydrogen bonds, and the geometries of the adsorbed NH3 molecules are plotted in Fig. 5. Two different mechanisms of stabilization are observed on this surface: H3N–H→O and O–H→NH3. The former mechanism occurs for the adsorption sites localized above the surface valley-like region. These adsorption minima are populated independently of the starting geometries, i.e. when NH3 approaches O(1)H or O(2)H, there is a proton shift from the surface OH groups to the ammonia molecule. After formation, the NH4+ cation migrates from the former OH site toward the valley region, where it is stabilized by multiple hydrogen-bonding interactions and favorable attractive electrostatic interactions (vide infra).

The ammonium ion (charge +0.87) forms two single hydrogen bonds with the O(2) atoms from two opposite hill regions with N···O distances of 2.70 Å and 2.72 Å and NHO angles of 173.2° and 174.3°. In addition, a weak trifurcated hydrogen-bonding interaction with one O(2) atom and two O(1) atoms from the bottom of the valley occurs. The N···O...
distances are 3.72 Å, 3.34 Å, and 3.30 Å and the NHO angles are 135.5°, 106°, and 105°, respectively. Moreover, the Mayer bond indices suggest that the N–H bonds (0.76–0.89) have higher covalences than the H–O bonds (0.1 for strong bonds, 0.01 for weak trifurcated bonds) do. Finally, small contributions to the adsorption energies also seem to be introduced by the interactions of NH4+ with surrounding V atoms. Although each of these interactions is characterized by a very small Mayer index (in the range of 0.007–0.016), the overall sum of the bond orders calculated for all three H atoms pointing into the valley equals 0.13, a value which is comparable with the strength of one hydrogen bond.

The latter O–H→NH3 mechanism is present only for the stable position localized in the “mountain”-like region of the (001) net plane, i.e., over the surface O(2)H group. Such a mode leads to the formation of a monodentate hydrogen bond (d(N⋯O) 2.71 Å, NHO angle 165.8°). The surface O–H acts as a proton donor (d(O–H)=1.04 Å, BO=0.69), forming a long hydrogen bond of moderate strength (d(H–N)=1.69, BO=0.15). The NH3 species remains almost neutral (+0.14), indicating an O–H→NH3 mechanism of hydrogen-bond formation. An inspection of the adsorption geometry at the O(2) site suggests that, in this case, the hydroxyl group is a proton donor; the H atom remains closer to the surface O atom than to the nitrogen atom from the ammonia molecule.

NH3 adsorption at the fully relaxed (010) V2O5 surface

The optimization of NH3 adsorption at the PBE/TZVP level of theory yielded qualitatively the same results as those obtained for RPBE/DZVP calculations, i.e., adsorption in the form of the NH4+ ion after proton transfer from the surface OH group to NH3 (see Table 3 and Table S3 in the ESM). As in previous (010) models, the most energetically favorable adsorption site was localized over O(1), the next most favorable was over O(3), O(2), and the least favorable was over O(2) (−1.58, −1.02, and −0.89 eV, respectively). The introduction of dispersion corrections did not change that trend (−1.72, −1.25, −1.16 eV, respectively). Similarly to RPBE models, the smallest D2 correction was observed for NH4+ adsorbed over V=O(1) ligands due to its relatively long distance from the V2O5 surface.

However, the application of a different optimization algorithm implemented in Turbomole, as well as a more diffuse basis set, led to some minor changes in the geometry of the NH4 ions that resulted in greater H-bond interaction (Fig. 6).

The tilt of the ammonia ion for the O(1),O(1) adsorption site becomes bigger than in RPBE model, which results in the presence of an additional bifurcated H-bond interaction of the third H atom with two O(1) atoms. This bifurcated bond is relatively weak, with H–O Mayer bond orders of 0.041 and 0.044 and H–O bond distances of 2.2 Å. Similarly, the ammonia is tilted over O(2) sites, which enables the formation of two weak H-bond contacts with O(3) oxygen atoms (BO = 0.036, d(H–O) = 2.33 Å). Finally, also in the case of NH4+ adsorption over O(3) sites, aside from two strong H-bonds with O(2) and O(3) oxygen atoms (H–O BO = 0.14 and 0.1, d(H–O)=1.74 and 1.78 Å, respectively), it was possible to detect the formation of one weak H-bond between a third hydrogen atom and an O(2) oxygen atom (BO=0.047, d(H–O)=2.1 Å).
Summing up, the calculations performed with almost full optimization of cluster geometry and with the application of the TZVP basis set led to similar results to those seen for models with only local geometry optimization and in which the DZVP basis set was applied. It seems that the main reason for the observed geometry differences stem from the different geometry optimization algorithms implemented in the Stobe and Turbomole codes.

NH₃ binding mechanism

There has been a long ongoing discussion in the literature concerning a form of adsorbed ammonia (see Table 1) [18]. Our results indicate that at low-index V₂O₅ surfaces, two types of adsorption over Brønsted acid (surface OH) centers may occur: (i) ammonia as a positively charged NH₄⁺ cation with a surface O site acting as a hydrogen acceptor, or (ii) ammonia as a neutral NH₃ molecule with a surface OH group acting as a hydrogen donor. Although hydrogen bonds are clearly the main force stabilizing the adsorbed ammonia, the local electrostatic characteristics of the surface where NH₃ contacts the OH group seem to determine the final form of the stabilized ammonia (i.e., either neutral or cationic).

Table 3 DFT (PBE/TZVP) and DFT+D2 corrected energies of ammonia adsorption over the (010) net plane and NH₃/NH₄⁺ charges calculated without and with H atoms adsorbed on the surface

| Adsorption site | O(1),O(1) | O(2), 2×O(3) | O(3),O(2), O(2) |
|----------------|-----------|--------------|----------------|
| E\textsubscript{ads} (NH₃) (eV) | −1.58 | −0.89 | −1.02 |
| E\textsubscript{ads} (NH₃) (kcal/mol\(^{−1}\)) | −36.4 | −20.6 | −23.5 |
| E\textsubscript{ads+D2corr} (eV) | −1.72 | −1.16 | −1.25 |
| (kcal/mol) | −39.8 | −26.7 | −28.8 |
| Mulliken population: | | | |
| Q(NH₃) | +0.48 | +0.49 | +0.53 |
| Q(NH₄⁺) | +0.75 | +0.79 | +0.81 |

Fig. 6 Geometries of ammonia adsorption on the (010) V₂O₅ model surface, calculated at the PBE/TZVP level of theory with full optimization of the surface. The NH₄⁺ cations are either stabilized by hydrogen bonds with an O(2) atom and two O(3) atoms, hydrogen bonds with one O(3) and two O(2) atoms, or two strong H-bond interactions with O(1) oxygen atoms and one weak bifurcated H-bond with two O(1) atoms. The geometries obtained for V₁₀O₃₁H₁₂ are translated to the model (010) surface for visualization purposes. The adsorption geometries on the V₁₀O₃₁H₁₂ are presented in Fig. S2 of the ESM.
This effect is especially visible in the case of a (001) low-index surface, which has varied electrostatic characteristics (i.e., some regions of positive and negative electrostatic potential are present) [65]. If the neutral NH$_3$ approaches Brønsted sites, it can accept a proton from the OH group to attain a positive charge. As a result, a decrease in the electrostatic potential of the adsorption sites is observed due to the local accumulation of a negative charge at the deprotonated Brønsted site (Table 4). Naturally, the electrostatic interaction becomes significant between the positively charged ammonium cation (Mulliken charge ca. 0.8) and the local negatively charged surface. As a result, the adsorption energy decreases further due to the attractive electrostatic interaction of the positive charge of the ammonium cation with the negative electrostatic potential produced by the surface.

For surface sites with a very stable or strong positive electrostatic potential that is insensitive to the OH protonation state, such a proton shift would result in an increase of the system energy due to the repulsive electrostatic interaction (i.e., an interaction of a positively charged surface with an NH$_4^+$ cation). Therefore, in such cases, ammonia remains in an almost neutral form (i.e., an NH$_3$ molecule with a small positive charge of ca. +0.2, which results from NH$_3$ acting as a hydrogen-bond acceptor), minimizing the increase in the total energy due to the unfavorable, repulsive electrostatic interactions. Similar conclusions have been drawn by Calatayud et al. [98], who have used electrostatic potential as a reactivity index for V$_2$O$_5$ gas-phase clusters as well as unsupported and TiO$_2$-supported (010) V$_2$O$_5$ surfaces. This approach allowed spatial mapping of the regions that are most susceptible to electrophilic attack and, in accordance with our results, pointed to the region between terminal (O1) oxygen atoms.

This observation can be studied in a more quantitative manner if one considers the change in the potential electrostatic energy upon shifting the proton from the OH site toward the approaching NH$_3$. Table 4 contains electrostatic potentials calculated at a distance of 2 Å above the hydrogen atom of each OH group for the studied surface. These potentials approximate the electrostatic environment affecting the NH$_3$ molecule approaching the surface (i.e., before the hydrogen bond is formed). The electrostatic potentials are determined for surfaces with an adsorbed hydrogen atom ($V^{OH}$) and a “bare” V$_2$O$_5$ surface ($V^{bare}$) without an adsorbed hydrogen atom. The change in potential energy $\Delta PE$ upon shifting the proton from the surface OH group to NH$_3$ is approximated as the difference between the electrostatic potential energy (PE) of NH$_4^+$ over a bare V$_2$O$_5$ surface and the PE of NH$_3$ over the OH group from the surface with an adsorbed hydrogen atom.

$$\Delta PE = PE(NH_4^+) - PE(NH_3) = V^{bare} q^{NH4^+} - V^{OH} q^{NH3},$$

where $q^{NH4^+}$ represents the average charge on the adsorbed ammonium cations (+0.86) and $q^{NH3}$ represents the charge on the adsorbed ammonia (+0.14) over the O(2) site at the (001) net plane. Thus, $\Delta PE$ describes the gain (or loss) in the electrostatic energy due to the transfer of a hydrogen from a surface OH group to an NH$_3$ molecule.

The transfer of a hydrogen in the form of a proton occurs when $\Delta PE$ is negative, ensuring strong electrostatic stabilization of the positively charged ammonium cation. In most of the cases studied, the change in electrostatic energy following the hydrogen shift is highly negative (from approximately −0.4 to −0.9 eV), which results in a thermodynamic preference for NH$_4^+$. However, for O(2) sites at a (001) surface, there is no energy gain connected with the hydrogen shift because the $\Delta PE$ attains a positive value (+0.03 eV). As a result, the ammonia is stabilized in its neutral form. Notably, at a (001) surface, the site of the proton shift is distant from the

### Table 4: The electrostatic characteristics of ammonia adsorption over the Brønsted sites of the (010), (100), and (001) V$_2$O$_5$ model surfaces

| Surface | (010) | (100) | (001) |
|---------|-------|-------|-------|
| Adsorption site | O(1) | O(2) | O(3) |
| Ads. species | NH$_4^+$ | NH$_4^+$ | NH$_4^+$ |
| $Q$ | 0.81 | 0.87 | 0.87 |
| $V^{OH}$ | −0.14 | 0.63 | 0.59 |
| $V^{bare}$ | −1.07 | −0.68 | −0.55 |
| PE(NH$_3$) | −0.02 | 0.10 | 0.09 |
| PE(NH$_4^+$) | −0.92 | −0.58 | −0.47 |
| $\Delta PE$ | −0.90 | −0.68 | −0.56 |

$Ad$s $s$pecies ($NH_4^+$/NH$_3$): form of ammonia moiety; $Q$: overall charge on the ammonia moiety; $V$: electrostatic potential (eV) calculated for the position of the N atom of the adsorbed ammonia over the hydrogenated (OH) and nonhydrogenated (bare) V$_2$O$_5$ model surfaces; $PE$: potential electrostatic energy (eV) of the adsorbed ammonia (PE(NH$_3$)) or the ammonium ion (PE(NH$_4^+$)) over the hydrogenated and nonhydrogenated surfaces, respectively; $\Delta PE$: difference between PE(NH$_4^+$) and PE(NH$_3$) in eV. The average charges used for the calculation of $\Delta PE$ are 0.86 for NH$_4^+$ and 0.16 for NH$_3$. 

© Springer
final, most favorable adsorption site. Regardless of the initial starting place of the NH$_3$ molecule (i.e., over O(1) or O$^\circ$(2)), the proton is shifted from the surface OH group. To probe the electrostatic influence of the surface on the proton shift process, the electrostatic potentials were calculated at distance of 2 Å above the H atoms adsorbed at the O$^\circ$(2) and O(1) sites. The results are collected in Table 4.

As observed from Table 4, the positive potential of the surface with the adsorbed H atom becomes negative (changing from 0.16 eV to −0.47 eV for the O(1) site and from 0.55 eV to −0.57 eV for the O$^\circ$(2) site). This result explains why ammonia becomes an ammonium cation at those sites. However, the vicinity of the deep negative potential well at the center of the valley (−1.58 eV for the NH$_3^+$ absorption site) attracts the cations to the most energetically favorable position.

Thus, the surface electrostatics influence the form of the stabilized ammonia. The local surface electrostatics of the spot at which ammonia contacts the surface determines whether the proton transfer will occur. If the proton is shifted, the ammonium cation can migrate further across the surface to maximize the electrostatic and hydrogen-bond interaction energies, as exemplified by a model of the adsorption over the O(1) and O$^\circ$(2) over (001) surface.

Quantitative modeling of adsorption energies

As shown above, the stabilization of ammonia over the Brønsted acid sites originates from the hydrogen bonds and is sensitive to the surface electrostatics. An interesting question arises as to whether it is possible to predict the strength of each adsorption site (i.e., the adsorption energy) based on a knowledge of the hydrogen-bond strength (derived only from geometry parameters) and on the local electrostatic potential. Theoretically, such a model would allow for the estimation of the relative importance of the forces (i.e., hydrogen bonds versus electrostatic) involved in the stabilization of ammonia over the V$_2$O$_5$ surface. Moreover, such a model would allow estimation of the adsorption site strength based solely on the geometry of the final structure of the V$_2$O$_5$–OH–NH$_3$ complex without the need to calculate the geometry and energy of the V$_2$O$_5$–OH reference model (thus shortening the calculation procedure). The usefulness of the electrostatic potential for predicting adsorption phenomena (such as interaction energies) has already been demonstrated by Tielens and Geerlings [99].

To build such a semiquantitative structure–property relationship (QSPR) model, each hydrogen-bond strength was described according to the methodology of the hydrogen bond analysis proposed by Jeffrey [100, 101], who studied a large number of hydrogen bonds and demonstrated that the energy of the particular bond varies between 0.2 and 40 kcal/mol$^1$ (which is up to ~1.7 eV). He then classified the hydrogen bonds into “strong,” “moderate,” and “weak” bonds based on several bond geometric parameters, such as

- The distance (H–A, in Å) between the proton (H) and the proton-acceptor group (A)
- An increased distance (Δ(D–H), in Å) between the proton (H) and the proton-donor group (D)
- The distance (D–A, in Å) between the proton-donor (D) and the proton-acceptor (A) groups
- The angle (α) of the N–H–O bond.

According to Jeffrey’s criteria, all of the necessary parameters were divided into “weak” (w), “moderate” (m), and “strong” (s) class contributions. Based on this concept, we selected a set of four parameters to describe the strength of each hydrogen bond responsible for the stabilization of ammonia at the V$_2$O$_5$ surfaces according to the scheme illustrated in Table S1 of the ESM and Table 5. Based on the categorization of these four parameters, we assigned a numerical value to each bond representing its strength, with 1 representing a weak, 2 a moderately strong, and 3 a strong hydrogen bond. Moreover, for hydrogen bonds of intermediate strength, we allocated intermediate values (for example, two moderate and two strong features results in a value of 2.5). Finally, for each site, the strengths of all identified hydrogen bonds were added together and this sum was used as a site hydrogen bond strength descriptor (SHBS).

The electrostatic energy was calculated as the product of the charge on the adsorbed species (NH$_3$ or NH$_3^+$) and the electrostatic potential of the respective surface (V$^\text{OH}$ or V$^\text{bare}$, respectively) at the atomic coordinates of the N atom of the adsorbed ammonia. The energy values obtained ranged from positive values (0.18 eV) for the (001) O(2) site to highly negative values for the valley adsorption site at the (001) surface (~1.54 eV). These extreme cases exemplify the effect of the electrostatic interaction on the overall energy (a decrease of E$^\text{adh}$ in the case of the positive electrostatic energy for the O(2) site at the (001) net plane and an increase of E$^\text{adh}$ in the case of the 4×O$^\circ$(2)O(2) site at the (001) net plane).

The results of the correlation analysis show a very high linear correlation of the adsorption energy E$^\text{adh}$ with the SHBS (R$=0.93$) and a moderate correlation with the electrostatic energy (R$=0.79$). Theoretically, both variables could be used to predict E$^\text{adh}$. However, these variables are nonorthogonal, i.e., they are linearly intercorrelated with R$=−0.82$. The collinearity indicates that multiple strong hydrogen-bonding interactions are present for sites with favorable (i.e., negative) electrostatic interactions. As a result, it is not possible to construct a QSPR model with these two variables; because of the collinearity problem, the electrostatic energy is statistically insignificant when used in one equation together with SHBS.

Therefore, it is not possible to independently estimate the influence of both variables on the adsorption energy. Because
more of the variance of the $E_{\text{ads}}$ value can be explained by SHBS ($R^2=0.87$), this descriptor can be used to approximate the energy using the following simple QSPR model:

$$E_{\text{ads}} = -0.21(\pm 0.037)\text{SHBS} - 0.20(\pm 0.17)$$

$$n = 7 \quad R^2 = 0.8609, \quad \text{corr. } R^2 = 0.8331, \quad F = 30.996, \quad p = 0.00258.$$  

The same model is obtained for DFT+D2 corrected adsorption energies ($R^2=0.87$, corr. $R^2=0.84404$, $F=33.472$, $p<0.00217$), where London dispersion forces are accounted for with a more negative constant ($-0.44$ instead of $-0.2$).

$$E_{\text{ads(DFT+D2)}} = -0.21(\pm 0.036)\text{SHBS} - 0.44(\pm 0.17.)$$

This result indicates that introducing DFT+D2 corrections on average does not cause any significant change to the observed trend.

The QSPR model demonstrates that higher hydrogen-bond strengths at the particular site result in lower adsorption energies. The quality of the model’s predictions is graphically presented on a scatter plot (see Fig. 7).

The apparent success of the applied hydrogen-bond strength index in predicting the adsorption energy clearly indicates two points: (i) the importance of these interactions in the stabilization of ammonia over V$_2$O$_5$ surfaces and (ii) the additivity of the hydrogen bonds at the particular adsorption site. However, as was demonstrated by statistical analysis, it is also important to take into account the fact that hydrogen bonds and surface electrostatic interactions are not separable.
independent phenomena. If a nondirectional positive electrostatic interaction exists, it allows for the formation of stronger, shorter hydrogen bonds. In contrast, when a repulsive interaction with the surface adsorbate occurs, the hydrogen bonds should be elongated, weakening the overall interaction. This relationship explains the high negative linear correlation that was observed between SHBS and the electrostatic energy at the adsorption site.

Conclusions

Based on the theoretical results, we can conclude that not only the saturated (010) but also the two unsaturated (001) and (100) surfaces are able to stabilize ammonia by adsorbing it at Brønsted acid sites, i.e., at OH surface groups. In all cases, the hydrogen bonds play a major role in this process.

Hydrogen bonds are formed via two different adsorption mechanisms. In the dominant scheme, a surface proton from the OH group is abstracted during ammonia adsorption and shifted toward the ammonia to become an NH$_4^+$ cation that serves as a “proton-donor” group in the newly created hydrogen bond. In the second scheme, no proton transfer is observed during the NH$_3$ adsorption; consequently, a surface hydroxyl species serves as the proton-donor group.

The local electrostatic interaction and the change in this interaction following proton transfer from the surface to the ammonia (when approaching the Brønsted site) appear to determine the adsorption mechanism. The electrostatic interactions between the catalyst surface and the adsorbing species also contribute to the overall stabilization, although it was not possible to evaluate the influence of these interactions on the adsorption energy independently of the input introduced by hydrogen bonding. The magnitude of this contribution strongly depends on the surface and is the largest for the negatively charged “valley” region of the (001) net plane (~1.97 eV). The adsorption energies of ammonia correlate very well with the hydrogen-bond strengths of the site. The strength of the hydrogen-bond stabilization can be derived only from geometrical features such as angles and atomic distances.

Finally, the results of our calculations fully confirm the previous predictions that the active sites for ammonia activation in the SCR mechanism are localized not only at saturated (010) sites but also at the unsaturated (001) and (100) V$_2$O$_5$ surfaces.

Acknowledgments The authors acknowledge the financial support of the Polish Ministry of Science and Higher Education under the research grant N204 024 31/0475 and computational grant MNiSW/IBM BC HS21/PAN/036/2012, as well as the financial support of the Marian Smoluchowski Krakow Research Consortium—a Leading National Research Centre KNOW.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Bosch H, Janssen F (1988) Formation and control of nitrogen oxides. Catal Today 2(4):369–379
2. Topsoe N-Y (1991) Characterization of the nature of surface sites on vanadia–titania catalysts by FTIR. J Catal 128(2):499–511
3. Cai Y, Ozkan US (1991) Vanadia/titania catalysts in selective catalytic reduction of nitric oxide with ammonia. Appl Catal 78(2):241–255
4. Topsoe NY, Topsoe H, Dumesic JA (1995) Vanadia/titania catalysts for selective catalytic reduction (SCR) of nitric oxide by ammonia: I. Combined temperature-programmed in-situ FTIR and on-line mass-spectroscopy studies. J Catal 151(1):226–240
5. Dumesic JA, Topsoe NY, Topsoe H, Chen Y, Slabiaik T (1996) Kinetics of selective catalytic reduction of nitric oxide by ammonia over vanadia/titania. J Catal 163(2):409–417
6. Lietti L, Forzatti P, Bregani F (1996) Steady-state and transient reactivity study of TiO$_2$-supported V$_2$O$_5$–WO$_3$–Fe–NOx catalysts: relevance of the vanadium–tungsten interaction on the catalytic activity. Ind Eng Chem Res 35(11):3884–3892
7. Lietti L, Alemany JL, Forzatti P, Busca G, Ramis G, Giannello E, Bregani F (1996) Reactivity of V$_2$O$_5$–WO$_3$/TiO$_2$ catalysts in the selective catalytic reduction of nitric oxide by ammonia. Catal Today 29(1–4):143–148
8. Duffy BL, Curry-Hyde HE, Cant NW, Nelson PF (1994) Isotopic labeling studies of the effects of temperature, water, and vanadia loading on the selective catalytic reduction of NO with NH$_3$ over vanadia–titania catalysts. J Phys Chem 98(29):7153–7161
9. Ramis G, Yi L, Busca G, Turco M, Kotur E, Willey RJ (1995) Adsorption, activation, and oxidation of ammonia over SCR catalysts. J Catal 157(2):523–535
10. Hu S, Apple TM (1996) $^{15}$N NMR study of the adsorption of NO and NH$_3$ on titania-supported vanadia catalysts. J Catal 158(1):112–124
11. Pinaeva LG, Suknev AP, Budneva AA, Paukshtis EA, Balzhimbaev BS (1996) On the role of oxygen in the reaction of NO reduction by NH$_3$ over monolayer V$_2$O$_5$–TiO$_2$ catalyst. J Mol Catal A Chem 112(1):115–124
12. Tronconi E, Lietti L, Forzatti P, Malloggi S (1996) Experimental and theoretical investigation of the dynamics of the SCR–DeNOx reaction. Chem Eng Sci 51(11):2965–2970
13. Qi G, Yang RT (2005) Low-temperature SCR of NO with NH$_3$ over noble metal promoted Fe–ZSM-5 catalysts. Catal Lett 100(3):243–246
14. Párvulescu VL, Grange P, Delmon B (1998) Catalytic removal of NO. Catal Today 46(4):233–316
15. Busca G, Lietti L, Ramis G, Berti F (1998) Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: a review. Appl Catal B 18(1–2):1–36
16. Bond GC, Forzatti P, Védrine JC (2000) General introduction: origins and objectives of the study. Catal Today 56(4):329–332
17. Coudurier G, Védrine JC (2000) EUROCAT oxide: an European noble metal promoted Fe–ZSM-5 catalyst. Surf Sci Rep 55(6–8):169–236
18. Calatayud M, Mgueu B, Minot C (2004) Modeling catalytic reduction of NO by ammonia over V$_2$O$_5$. Surf Sci Rep 55(6–8):169–236
19. Tronconi E, Nova I, Ciardelli C, Chatterjee D, Weibel M (2007) Redox features in the catalytic mechanism of the “standard” and “fast” NH$_3$–SCR of NOx over a V-based catalyst investigated by dynamic methods. J Catal 245(1):1–10
20. Goo JH, Irfan MF, Kim SD, Hong SC (2007) Effects of NO_{2} and SO_{2} on selective catalytic reduction of nitrogen oxides by ammonia. Chemosphere 67(4):718–723

21. Koebel M, Madia G, Elsener M (2002) Selective catalytic reduction of NO and NO_{2} at low temperatures. Catal Today 73(3–4):239–247

22. Koebel M, Madia G, Raimondi F, Wokaun A (2002) Enhanced reoxidation of vanadia by NO_{2} in the fast SCR reaction. J Catal 209(1):159–165

23. Madia G, Koebel M, Elsener M, Wokaun A (2002) Side reactions in the selective catalytic reduction of NO with various NO_{x} fractions. Ind Eng Chem Res 41(16):4028–4015

24. Inomata M, Miyamoto A, Murakami Y (1980) Mechanism of the reaction of NO and NH_{3} on vanadium oxide catalyst in the presence of oxygen under the dilute gas condition. J Catal 62(1):140–148

25. Miyamoto A, Yamazaki Y, Hattori T, Inomata M, Murakami Y (1982) Study on the pulse reaction technique: VI. Kinetics of the reaction of NO with NH_{3} on a V_{2}O_{5} catalyst. J Catal 74(1):144–155

26. Miyamoto A, Kobayashi K, Inomata M, Murakami Y (1982) Nitrogen-15 tracer investigation of the mechanism of the reaction of nitric oxide with ammonia on vanadium oxide catalysts. J Phys Chem 86(15):2945–2950

27. Lietti L, Svachula J, Forzatti P, Busca G, Ramis G, Bregani P (1993) Surface and catalytic properties of vanadia–titania and tungstasphene systems in the selective catalytic reduction of nitrogen oxides. Catal Today 17(1–2):131–139

28. Lietti L, Ramis G, Berti F, Toleda G, Robba D, Busca G, Forzatti P (1998) Chemical, structural and mechanistic aspects on NOx SCR over commercial and model oxide catalysts. Catal Today 42(1–2):101–116

29. Lietti L, Nova I, Tronconi E, Forzatti P (1998) Transient kinetic study of the SCR–DeNOx reaction. Catal Today 45(1–4):85–92

30. Casagrande L, Lietti L, Nova I, Forzatti P, Baiker A (1999) SCR of NO by NH_{3} over TiO_{2}–supported V_{2}O_{5}–MoO_{3} catalysts: reactivity and redox behavior. Appl Catal B 21(3):424–428

31. Odriozola JA, Heinemann H, Somorjai GA, de la Banda JFG, Pereira P (1989) AES and TDS study of the adsorption of NH_{3} and NO on V_{2}O_{5} and TiO_{2} surfaces: mechanistic implications. J Catal 119(1):71–82

32. Odriozola JA, Soria J, Somorjai GA, Heinemann H, Garcia de la Banda JF, Lopez Granados M, Coesa JC (1991) Adsorption of nitric oxide and ammonia on vanadia–titania catalysts: ESR and XPS studies of adsorption. J Phys Chem 95(1):240–246

33. Centeno MA, Carrizoza I, Odriozola JA (1998) In situ DRIFTS study of the SCR reaction of NO with NH_{3} in the presence of O_{2} over lanthanide-doped V_{2}O_{5}/Al_{2}O_{3} catalysts. Appl Catal B 19(1):63–77

34. Janssen FJG, Van den Kerkhof FMG, Bosch H, Ross JRH (1987) Mechanism of the reduction of nitric oxide, ammonia, and oxygen over vanadia catalysts. I. The role of oxygen studied by way of isotopic transients under dilute conditions. J Phys Chem 91(23):5921–5927

35. Janssen FJG, Van den Kerkhof FMG, Bosch H, Ross JRH (1987) Mechanism of the reaction of nitric oxide, ammonia, and oxygen over vanadia catalysts. II. Isotopic transient studies with oxygen-18 and nitrogen-15. J Phys Chem 91(27):6633–6638

36. Ramis G, Yi L, Busca G (1996) Ammonia activation over catalysts for the selective catalytic reduction of NOx and the selective catalytic oxidation of NH_{3}. An FT-IR study. Catal Today 28(4):373–380

37. Schneider H, Tschudin S, Schneider M, Wokaun A, Baiker A (1994) In situ diffuse reflectance FTIR study of the selective catalytic reduction of NO by NH_{3} over vanadia–titania aerogels. J Catal 147(1):5–14

38. Schneider H, Tschudin S, Schneider M, Wokaun A, Baiker A (1994) Effect of crystal morphology in selective catalytic reduction of nitric oxide over V_{2}O_{5} catalysts. Appl Catal A 96(2):365–381

39. Ozkan US, Cai Y, Kumtheekar MW (1993) Effect of crystal morphology in selective catalytic reduction of nitric oxide over V_{2}O_{5} catalysts. J Catal 142(1):182–197

40. Ozkan US, Cai YP, Kumtheekar MW (1994) Investigation of the reaction pathways in selective catalytic reduction of NO with NH_{3} over V_{2}O_{5} catalysts: isotopic labeling studies using ^{15}O_{2}, ^{15}NH_{3}, ^{15}NO, and ^{15}N^{18}O. J Catal 149(2):390–403

41. Gasior M, Haber J, Machtej T, Czepe T (1988) Mechanism of the reaction NO+NH_{3} on V_{2}O_{5} catalysts. J Mol Catal 43(3):359–369

42. Takagi-Kawai M, Kawai T, Soma M, Onishi T, Tamura K (1979) Reply to Akira Miyamoto et al. J Catal 57(3):528–528

43. Takagi M, Kawai T, Soma M, Onishi T, Tamura K (1977) The mechanism of the reaction between NOx and NH_{3} on V_{2}O_{5} in the presence of oxygen. J Catal 50(3):441–446

44. Takagi M, Kawai T, Soma M, Onishi T, Tamura K (1976) Mechanism of catalytic reaction between nitric oxide and ammonia on vanadium pentoxide in the presence of oxygen. J Phys Chem 80(4):430–431

45. Went GT, Leu L-J, Rosin RR, Bell AT (1992) The effects of structure on the catalytic activity and selectivity of V_{2}O_{5}/TiO_{2} for the reduction of NO by NH_{3}. J Catal 134(2):492–505

46. Topsoe NY, Dumesic JA, Topsoe H (1995) Vanadia–titania catalysts for selective catalytic reduction of nitric oxide by ammonia: I.1. Studies of active sites and formulation of catalytic cycles. J Catal 151(1):241–252

47. Topsoe NY, Dumesic JA, Topsoe H (1995) Theoretical insight into the nature of ammonia adsorption on vanadia–titania catalysts with model catalysts: experiments combined with DFT calculations. J Mol Catal A Chem 432(3):263–275

48. Anstrom M, Dumesic JA, Topsøe N-Y, Dumesic JA (2002) Theoretical and experimental studies of biochemical aspects of the SCR reaction on vanadium oxide catalysts. J Catal 213(2):148–155

49. Andersson A (1982) An oxidized surface state model of vanadium pentoxide/aluminum oxide catalysts. J Catal 64:259–278

50. Yuan R-M, Fu G, Xu X, Wan H-L (2011) Bronsted-NH_{4}^{+} mechanism versus nitrite mechanism: new insight into the selective catalytic reduction of NO by NH_{3}. Phys Chem Chem Phys 13(2):453–460

51. Sun C, Dong L, Yu W, Liu L, Li H, Gao F, Dong L, Chen Y (2011) Promotion effect of tungsten oxide on SCR of NO with NH_{3} for the V_{2}O_{5}–WO_{3}/TiO_{2} model catalyst: experiments combined with DFT calculations. J Mol Catal A Chem 346(1–2):29–38

52. Topsoe NY, Dumesic JA, Topsoe H (2003) Density functional theory studies of mechanistic aspects of the SCR reaction on vanadium oxide catalysts. J Catal 213(2):115–125

53. Anstrom M, Dumesic JA, Topsøe N-Y (2002) Theoretical insight into the nature of ammonia adsorption on vanadia–titania-based catalysts for SCR reaction. Catal Lett 78(1):281–289

54. Koobayashi Y, Tajima N, Nakano H, Hirao K (2004) Selective catalytic reduction of nitric oxide by ammonia: the activation mechanism. J Phys Chem B 108(33):12264–12266

55. Kaschovskaya NA, Mikheeva EP, Zhidomirov GM (2002) Cluster molecular modeling of strong interaction for VOx/TiO2 supported catalysts. J Mol Catal A Chem 178(1–2):191–198

56. Soyer S, Uzun A, Senkan S, Oral I (2006) A quantum chemical study of nitric oxide reduction by ammonia (SCR reaction) on V_{2}O_{5} catalyst surface. Catal Today 118(3–4):268–278

57. Gilaroldi F, Weber J, Baiker A (1997) Density functional investigation of the mechanism of the selective catalytic reduction of NO by NH_{3} over vanadium oxide model clusters. Int J Quantum Chem 61(4):683–688

58. Gilaroldi F, Weber J, Baiker A (1997) Mechanism of the vanadium oxide-catalyzed selective reduction of NO by NH_{3}. A quantum chemical modeling. J Phys Chem A 101(34):6069–6076
