Theoretical insight into the nature of ammonia adsorption on vanadia-based catalysts for SCR reaction

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Density functional theory (DFT) calculations were carried out on monomeric and oligomeric vanadium oxide clusters to probe the factors leading to the formation of NH_4 species from the adsorption of ammonia. The interaction of ammonia with monomeric vanadium oxide clusters leads to the formation of hydrogen-bonded NH_3 species, with energy changes for ammonia adsorption near -50 kJ/mol. The interaction of ammonia with oligomeric vanadium oxide clusters leads to the formation of bidentate NH_4 species, where the ammonium cation is coordinated between two V=O groups on adjacent vanadium cations. The energy change for ammonia adsorption in this mode is near -100 kJ/mol. Adsorption of ammonia as NH_4 species was not observed when the oligomeric vanadium oxide clusters were reduced by addition of hydrogen atoms, *i.e.*, in clusters where the formal oxidation state of the vanadium cations was 4+. Based on our findings, a model for the generation of Brønsted acidity through the interaction of vanadium oxide oligomers with the titanium oxide support is proposed.

KEY WORDS: vanadia catalyst; ammonia adsorption; NO reduction

1. Introduction

The selective catalytic reduction (SCR) of NO by NH_3 over vanadia/titania catalysts is generally considered to take place via reaction between adsorbed ammonia and weakly-adsorbed NO [1–7]. Ammonia adsorbs on Lewis acid sites to give coordinated NH_3 species, as well as on Brønsted acid sites to give NH_4 species. Topsøe *et al.* [5] studied a series of vanadia/titania catalysts with vanadia loadings up to 6 wt%, and these authors found that the amount of ammonia adsorbed as NH_4 under SCR reaction conditions was not linearly related to the vanadia loading. In particular, significant amounts of NH_4 species were favored on catalysts with higher loadings of vanadia. A similar study performed by Schneider *et al.* [6] showed that formation of NH_4 species is favored on catalysts with higher loadings of vanadia. Results from theoretical calculations of the interaction of NH_3 with hydrogen atoms on vanadium oxide clusters [8,9] and slabs [10] indicate that ammonia can abstract a hydrogen atom to form NH_4 species that are coordinated to two vanadyl (V=O) centers.

The adsorption of ammonia to give NH_4 species has been extensively modeled *via* quantum chemical calculations over various silica–alumina clusters. An early study by Teunissen *et al.* [11] indicated that NH_4 species adsorb as bidentate or tridentate species over a $H_2Al(OH)_2$ cluster whereas monodentate NH_4 species are unstable. A study by Greatbanks *et al.* [12] using density functional theory on a silica–alumina trimer showed that ammonia adsorbs preferentially as a bidentate NH_4 species between two oxygen atoms bonded to the same aluminum atom. Kyrlidis *et al.* [13] employed a model of H-ZSM5 consisting of a silica–alumina pentamer to model ammonia adsorption, and these authors found that ammonia adsorbs as bidentate or tridentate NH_4 species. Similar studies have shown that ammonia adsorbs as a bidentate species over faujasite [14–16], mordenite [17], ZSM-5 [17,18], as a bidentate or tridentate species over chabazite [16,18], and as a bidentate or tetradentate species over MFI [17,18]. These results compare well with infrared spectroscopic results, which indicate that NH_4 species adsorb with bidentate and tridentate structures in ZSM-5, H-Y, mordenite, and H-beta zeolites [19].

In the present paper, we will probe various adsorption geometries and energies for the interaction of ammonia with hydrogen atoms present on clusters representing vanadium oxide, with the aim of addressing various factors controlling the formation of Brønsted acid sites that interact with ammonia to form NH_4 species.

2. DFT calculation methods

Quantum chemical calculations employing density functional theory were conducted to probe the energetics for various types of vanadium oxide clusters and to study the interaction of NH_3 with hydrogen atoms on different types of oxygen atoms in these clusters. The clusters used in this study were initially constructed from the crystal

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structure [20] of V_2O_5. The desired number of adjacent vanadium atoms was selected, along with the neighboring oxygen atoms, to complete the coordination environment of the vanadium cations. Hydrogen atoms were then added to maintain charge neutrality for the cluster, assuming that all species existed in their formal oxidation states. These hydrogen atoms were thus added to form terminal hydroxyl groups (–OH) or water molecules ($-OH_2$) where necessary.

The DEE calculations were carried out using DEC workstations with the Jaguar software package (Schrodinger, Inc.) The chosen DFT method uses a hybrid method employing Becke's three-parameters approach, B3LYP [21]. This functional combines the exact HF exchange, Slater's local exchange functional, and Becke's 1988 non-local gradient correction to the exchange functional with the correlation functionals of Vosko–Wilk–Nusair (VWN) and Lee–Yang–Parr (LYP).

The basis set employed in all calculations (LACVP**) uses an effective core potential on all V and Ti atoms, developed at Los Alamos National Laboratory by Hay and Wadt [22]. The electrons treated explicitly on V and Ti are the outermost core and valence electrons ($3s^22p^64s^23d^3$ for V, $3s^22p^64s^23d^2$ for Ti). The H, N, and O atoms have been treated with the 6–31G** basis set, with all electrons being treated explicitly. Selected clusters were optimized in higher (triplet, quadruplet) multiplicity states; however, in each case the cluster with the lowest possible multiplicity (singlet or doublet) had the lowest energy.

The energy change for ammonia adsorption on each cluster was determined as follows:

$$\Delta E_{\text{ads}} = (E_{\text{VNH}_3}) - (E_{\text{V}} + E_{\text{NH}_3})$$

where E_{VNH_3} is the energy of the ammonia-cluster surface complex, and E_{V} and E_{NH_3} represent the energies of the $V_xO_yH_z$-cluster and gas-phase ammonia, respectively.

3. Results

Various clusters were constructed to investigate the geometry and energy of adsorption of ammonia on vanadium oxide. A VO_4H_3 cluster, shown in figure 1(a), was used to investigate the nature of ammonia adsorption on tetrahedrally coordinated vanadium oxide monomers. All atoms in the cluster as well as those belonging to NH_3 were allowed to fully relax during optimization. Ammonia was found to adsorb as H-bonded NH_3 species on vanadia monomers, with an energy change of adsorption equal to −59 kJ/mol.

Previous studies [23–25] indicate that at low surface concentrations, vanadium oxide exists primarily as monomeric VO_x or VO_4 tetrahedra on the surface of titania. However, at higher surface loadings, polymeric species predominate, in which the VO_4 tetrahedra are linked by V–O–V bonds. Previous theoretical studies [8–10] show that ammonia adsorbs as NH_4 species between two vanadyl groups (V=O) of these polymeric species. Accordingly, the clusters shown in figure 1 containing 1 and 2 vanadium atoms were constructed to probe the energetics for the oligomerization of vanadium oxide clusters. These clusters are based on the following stoichiometries: $VO_4H_3{\cdot}H_2O$ and $V_2O_7H_4{\cdot}(H_2O)_2$. The $V_2O_7H_4{\cdot}(H_2O)_2$ cluster was initially constructed by taking two vanadium atoms from a (010) plane of V_2O_5, including all oxygen atoms within the plane that are directly bonded to the two vanadium atoms. Hydrogen atoms were then added to the cluster to maintain charge neutrality. Except as noted, the clusters were optimized with the following geometric constraints: all O[1]–V–V angles were constrained at 90°, and all O[1]–V–V–O[1] dihedral angles were constrained at 0°. In addition, the dihedral angles of all terminal hydrogen atoms were fixed to prevent hydrogen bonding.

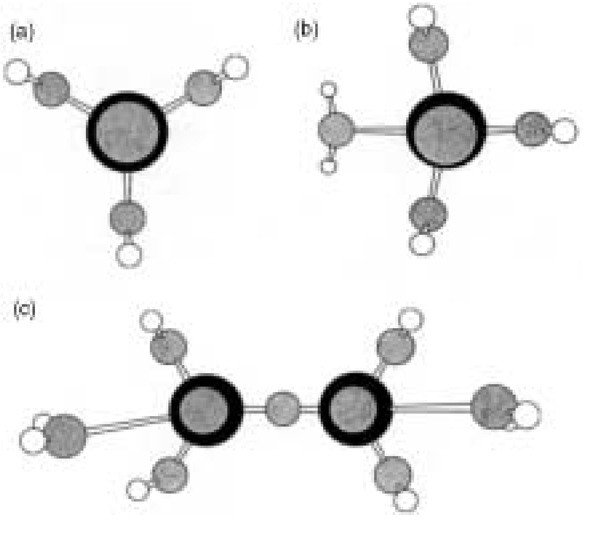


Figure 1. (a) VO_4H_3 cluster; (b) $VO_4H_3{\cdot}H_2O$ cluster; and (c) $V_3O_7H_4{\cdot}(H_2O)_2$ cluster. The following coloration is used in this and all subsequent figures: H, white; O, gray; V, black.

Values for the different V–O distances in the $VO_4H_3{\cdot}H_2O$ and $V_2O_7H_4{\cdot}(H_2O)_2$ clusters are presented in table 1. It can be seen in this table that the $V-OH_2$ distances in the $VO_4H_3{\cdot}H_2O$ and $V_2O_7H_4{\cdot}(H_2O)_2$

Table 1
V–O distances (pm) in vanadium oxide clusters

	Bond distance (pm)
$VO_4H_3{\cdot}H_2O$-cluster	
V=O	158
V–OH	177–178
$V-OH_2$	360
$V_2O_7H_4{\cdot}(H_2O)_2$-cluster	
V=O	157–158
V–OH	177–178
V–O–V	178
$V-OH_2$	321–327

clusters are very long: 360 pm for the $VO_4H_3{\cdot}H_2O$ cluster, and 325 pm for the $V_2O_7H_4{\cdot}(H_2O)_2$ cluster. Accordingly, H_2O is expected to be bonded rather weakly to the clusters. This result is confirmed by conducting DFT calculations using VO_4H_3 and $V_2O_7H_4$ clusters and then calculating the energy changes for the reactions:

$$VO_4H_3{\cdot}H_2O \rightarrow VO_4H_3 + H_2O$$

$$V_2O_7H_4{\cdot}(H_2O)_2 \rightarrow V_2O_7H_4 + 2H_2O.$$

The binding energies for water adsorption were calculated to be approximately 20 kJ/mol for both the $VO_4H_3{\cdot}H_2O$ and $V_2O_7H_4{\cdot}(H_2O)_2$ clusters.

The energy changes for the following oligomerization reaction were calculated to be −10 kJ/mol:

$$VO_4H_3{\cdot}H_2O + VO_4H_3{\cdot}H_2O \rightarrow$$

$$V_2O_7H_4{\cdot}(H_2O)_2 + H_2O.$$

Thus, the inter-conversion between the $VO_4H_3{\cdot}H_2O$ and $V_2O_7H_4{\cdot}(H_2O)_2$ clusters is energetically neutral. Accordingly, this result suggests that $VO_4H_3{\cdot}H_2O$ as well as $V_2O_7H_4{\cdot}(H_2O)_2$ clusters can exist on the catalyst surface, depending on the vanadia loading. We also note that the coordination environment of the vanadium atoms in the $V_2O_7H_4{\cdot}(H_2O)_2$ cluster becomes nearly tetrahedral. This nearly tetrahedral structure observed under full optimization is in agreement with published V-51 NMR [26] and EXAFS [27] results, indicating that the vanadium cations in surface vanadia structures are four-coordinated, with one terminal V=O bond and three bridging V−O bonds.

In view of previous IR spectroscopic results [3–5] where NH_4 species were observed on vanadia surfaces, the adsorption of ammonia on vanadia dimers was investigated by adding a hydrogen atom to the $V_2O_7H_4{\cdot}(H_2O)_2$ cluster to form $H\text{-}V_2O_7H_4{\cdot}(H_2O)_2$ clusters, as shown in figure 2. In these clusters of figure 2(a) and (b), we note that the H atom is attached to an oxygen atom that is coordinated to 1 vanadium cation (O[1]) or coordinated to 2 vanadium cations (O[2]), respectively. As with the VO_4H_3 monomer, the calculations show that ammonia adsorbs on these clusters as H-bonded NH_3 species, with adsorption energy changes near −50 kJ/mol. Thus, neither of these clusters leads to the formation of NH_4 species upon interaction with ammonia.

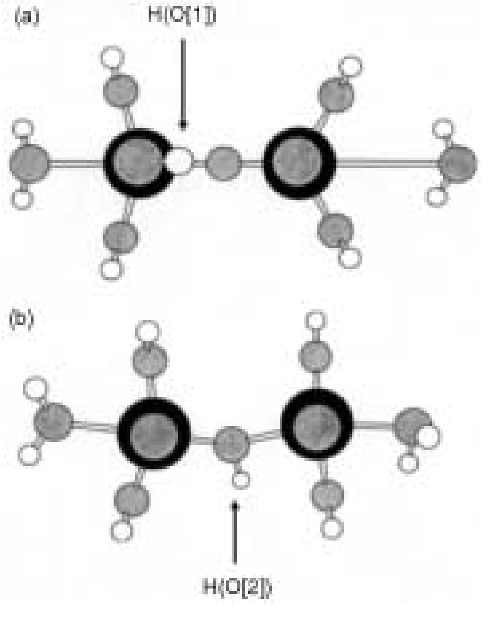


Figure 2. $V_2O_7H_4{\cdot}(H_2O)_2$ cluster after addition of H atom at (a) the O[1] position and (b) the O[2] position.

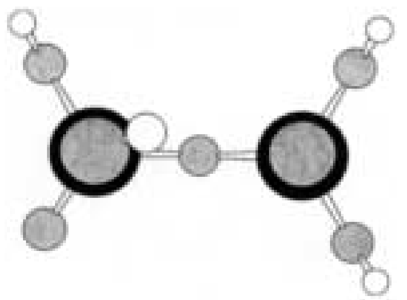


Figure 3. $V_2O_7H_4$ cluster.

As noted above, results from V-51 NMR [26] and EXAFS [27] studies indicate that the coordination state of vanadium atoms in supported vanadium oxide is primarily tetrahedral. To investigate the adsorption of NH_3 on tetrahedrally coordinated polymeric vanadia (*i.e.*, without coordinating water molecules), a $H\text{-}V_2O_7H_4$ cluster was employed. Ammonia was found to adsorb on the $H\text{-}V_2O_7H_4$ cluster as H-bonded NH_3 species, with an energy change of −64 kJ/mol.

The adsorption of NH_3 on the $V_2O_7H_4$ cluster shown in figure 3 was also studied. This cluster was obtained from the $H\text{-}V_2O_7H_4$ cluster by removing a hydrogen atom from a terminal VOH group. The formal oxidation state of the vanadium cations in this $V_2O_7H_4$ cluster is thus higher than in the $H\text{-}V_2O_7H_4$ cluster. Ammonia was found to adsorb on the $V_2O_7H_4$ cluster as H-bonded NH_3 species, with an energy of −72 kJ/mol. This adsorption energy change is thus in agreement with the value for ammonia coordinated to the $H\text{-}V_2O_7H_4$ cluster.

Several other clusters containing two vanadium atoms were constructed to address specifically the factors responsible for the adsorption of ammonia to form NH_4 species. One such cluster, denoted as $V_2O_9H_8$, is shown in figure 4(a). Interaction of ammonia with the $V_2O_9H_8$ cluster formed NH_4 species, and the resulting structure is shown in figure 4(b). When NH_3 was adsorbed between the two O[1] atoms, as in figure 4(b), the cluster was stable. However, optimization of the cluster shown in figure 4(a) resulted in decomposition of the cluster to $(OH)_3V{=}O$ and $V(OH)_5$. Accordingly, the cluster shown in figure 4(a) was optimized from the cluster shown in figure 4(b) with the positions of the vanadium atoms and the O[2] atoms kept fixed to prevent decomposition. The O[1]−H and O[2]−H bond lengths in the cluster shown in figure 4(a) are 97.8 pm and 97.1 pm, respectively, suggesting that

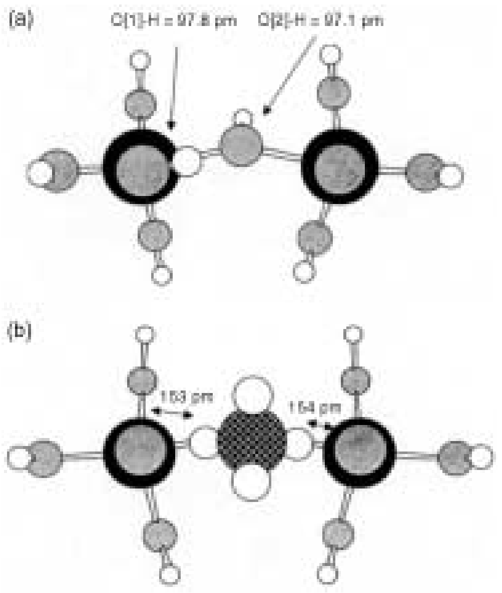


Figure 4. $V_2O_9H_8$ cluster (a) before NH_3 adsorption at O[1] and (b) after NH_3 adsorption at O[1].

the O[1] atom may be a slightly stronger hydrogen donor than the O[2] atom. The Mulliken charges on the hydrogen atoms of the O[1]–H and O[2]–H groups are +0.384 e and +0.358 e respectively, which also suggests that the hydrogen atom at O[1] is more acidic than the hydrogen atom at O[2]. The transfer of the two hydrogen atoms from the cluster shown in figure 1(c) is endothermic by 201 kJ/mol. From figure 4(b), it can be seen that the NH_4 species is symmetrically coordinated to two O[1] groups, with H–O bond lengths of 153 and 154 pm. The energy change for adsorption of ammonia in this fashion is −111 kJ/mol. The Mulliken charge on the NH_4 species is +0.807 e, suggesting that NH_3 adsorbs at O[1]–H sites as NH_4^+.

Optimization of the clusters shown in figure 4(a) and (b) with the angles and dihedral angles of the VOH groups held fixed resulted in stable dimer species which are geometrically similar to those shown in figure 4(a) and (b). When optimized in this fashion, the cluster in figure 4(a) adsorbed ammonia as a NH_4 species with an adsorption energy of −135 kJ/mol.

Gilardoni *et al.* [8,9] employed a $V_2O_9H_7$ cluster to model ammonia adsorption on vanadia dimers. The cluster with a hydrogen atom at the O[1] position and the resulting structure formed when ammonia was adsorbed on the cluster are shown in figure 5(a) and (b). It can be seen in figure 5(b) that ammonia adsorbs as NH_4 species coordinated between the two O[1] atoms, and the energy change of adsorption is equal to −129 kJ/mol. This energy change is somewhat higher than the DFT-calculated literature value [8] of −110 kJ/mol, and it is significantly more exothermic than the heat of adsorption of −72 kJ/mol observed by Srnak *et al.* [28] for the adsorption of NH_3 on Brønsted acid sites as NH_4 species. The O[1]–H bond length is 97.6 pm, and the Mulliken charge on the H atom is +0.385 e. The bonding of NH_4 to the cluster is symmetric, with O–H bond lengths of 158 pm and 159 pm. Optimization of the clusters shown in figure 5(a) and (b) with the VOH angles and dihedral angles held constant (*cf.* Gilardoni *et al.* [8,9]) resulted in structures which are geometrically similar to those shown in figure 5(a) and (b). When optimized in this fashion, the cluster shown in figure 5(a) adsorbed ammonia as a NH_4 species with an adsorption energy change of −112 kJ/mol. The Mulliken charge on the NH_4 species is +0.802 e, suggesting that ammonia adsorbs as NH_4^+ species at O[1]–H sites.

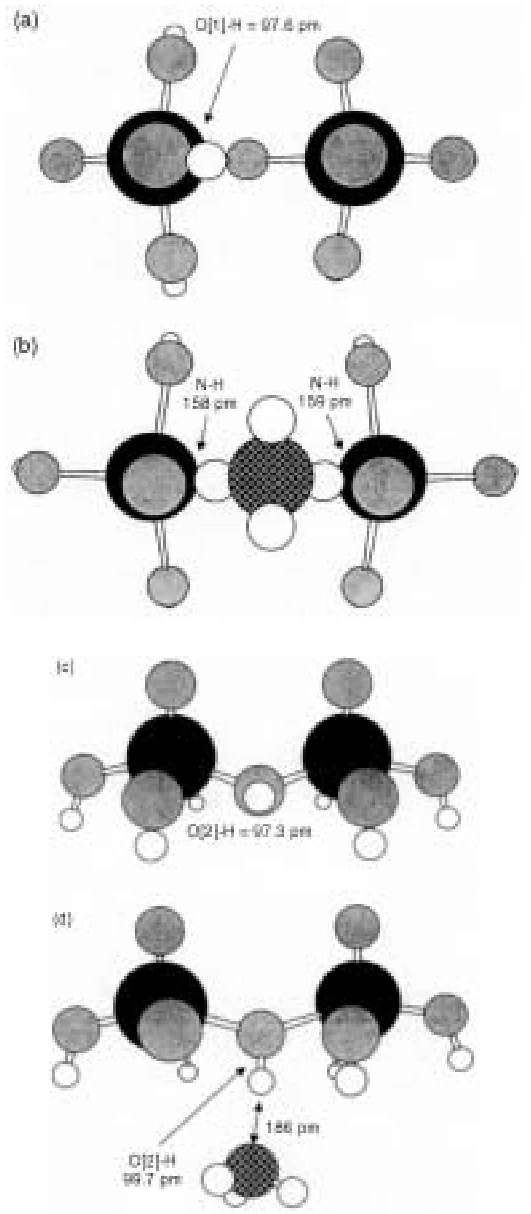


Figure 5. $V_2O_9H_7$ cluster (a) before NH_3 adsorption at O[1]; (b) after NH_3 adsorption at O[1]; (c) before NH_3 adsorption at O[2]; and (d) after NH_3 adsorption at O[2]. Nitrogen is colored gray and has checkerboard hatching in this and all subsequent figures. Some hydrogen atoms are obscured from view.

The cluster with a hydrogen atom at the O[2] position and the resulting structure formed when ammonia was adsorbed on the cluster are shown in figure 5(c) and (d). Full optimization of this cluster resulted in the decomposition of the cluster to $(OH)_3V{=}O$ and $(OH)V{=}O$. In order to keep the cluster from splitting apart, the clusters shown in figure 5(c) and (d) were optimized while constraining the two V–O[2] bond distances to be equal. The energy of the cluster shown in figure 5(c) is +21 kJ/mol relative to the cluster formed by adding the hydrogen atom to the O[1] position (figure 5(a)). The O[2]–H bond length in this cluster is 97.3 pm, which is shorter than the O[1]–H bond length of the cluster shown in figure 5(a). The Mulliken charge on the hydrogen atom of the O[2]–H group is +0.362 e, which is in agreement with the shorter O[2]–H bond length as compared to the O[1]–H bond length. Ammonia adsorbs as H-bonded NH_3 species at the O[2] position, with an adsorption energy change of −58 kJ/mol. The N–H bond length is 186 pm, and the O[2]–H bond length 99.7 pm. The Mulliken charge on the hydrogen bonded NH_3 species is +0.081 e, suggesting that ammonia adsorbs on O[2]–H as a neutral NH_3 species.

Optimization of the clusters shown in figure 5(c) and (d) with the VOH angles and dihedral angles held constant resulted in stable vanadia dimer species which are geometrically similar to those shown in figure 5(c) and (d). When optimized in this fashion, the cluster shown in figure 5(a) adsorbed ammonia as a hydrogen bonded NH_3 species with an adsorption energy of −59 kJ/mol.

The possibility of adsorbing NH_4 between the O[1] and O[2] atoms of the cluster proposed by Gilardoni *et al.* [8] was also investigated. During geometry optimization, however, the NH_4 species was found to move to a position in which the NH_4 group was coordinated to two O[1] atoms (as in figure 5(b)).

The $V_2O_9H_7$ cluster was also used to model the kinetics of hydrogen atom transfer between neighboring O[1] atoms as well as between O[1] and O[2] atoms. In order to minimize the impact of the arrangement of the VOH groups on the energy of the cluster, the angles and dihedral angles of the $V_2O_9H_7$ cluster were fixed during optimization. The positions of the two vanadium atoms and the O[1] and O[2] atoms were completely optimized. Upon reoptimization, the energy of the O[2]–H cluster relative to the O[1]–H cluster decreased to +9 kJ/mol. The approximate transition state for hydrogen transfer was found by constraining the newly-forming O[1]–H or O[2]–H bond at successively shorter bond lengths and re-optimizing the cluster as described above. The activation energy barrier for the transfer of the hydrogen atom from a O[1] to another O[1] atom was calculated to be 28 kJ/mol, and the energy barrier for the transfer of the hydrogen atom from a O[1] to the O[2] atom was calculated to be 148 kJ/mol. These activation energy barriers calculated for the $V_2O_9H_7$ cluster compare well with previous results reported for hydrogen transfer for the $H\text{-}V_2O_7H_4{\cdot}(H_2O)_2$ cluster [25].

As noted above, the $V_2O_9H_8$ cluster derived from the $V_2O_7H_4{\cdot}(H_2O)_2$ cluster by dissociating two water molecules, forms NH_4 species upon interaction with ammonia; therefore, this cluster appears to model the Brønsted acid sites on a vanadia catalyst. However, the high endothermic energy change of 200 kJ/mol for dissociation of the two water molecules is cause for concern. Accordingly we have studied whether a Brønsted acid site can be formed from the interaction of a Ti–OH group with a $V_2O_7H_4$ cluster. In these clusters, the H atom of the Ti–OH group is transferred to the $V_2O_7H_4$ cluster, and a Ti–O–V linkage is formed. The TiV_2 clusters formed from the condensation of a $Ti(OH)_4$ moiety with the $V_2O_7H_4$ cluster are shown in figure 6(a) and (b). The transfer of the hydrogen atom to the O[1] position (figure 6(a)) is favored over transfer to O[2] (figure 6(b)) by 63 kJ/mol. The O[1]–H bond length (97.2 pm) is slightly shorter than the O[2]–H bond length (97.4 pm), which is in agreement with the greater stability of the cluster when the hydrogen atom is transferred to O[1]. Importantly, this transfer of a hydrogen atom from the $Ti(OH)_4$ moiety to the O[1] position of the $V_2O_7H_4$ cluster is endothermic by only 65 kJ/mol, and this value is much more favorable than the energy change for transfer of a hydrogen atom to the O[1] position from an adsorbed H_2O molecule (*i.e.*, 100 kJ/mol). Given that the $Ti(OH)_4$ moiety is a primitive approximation for the

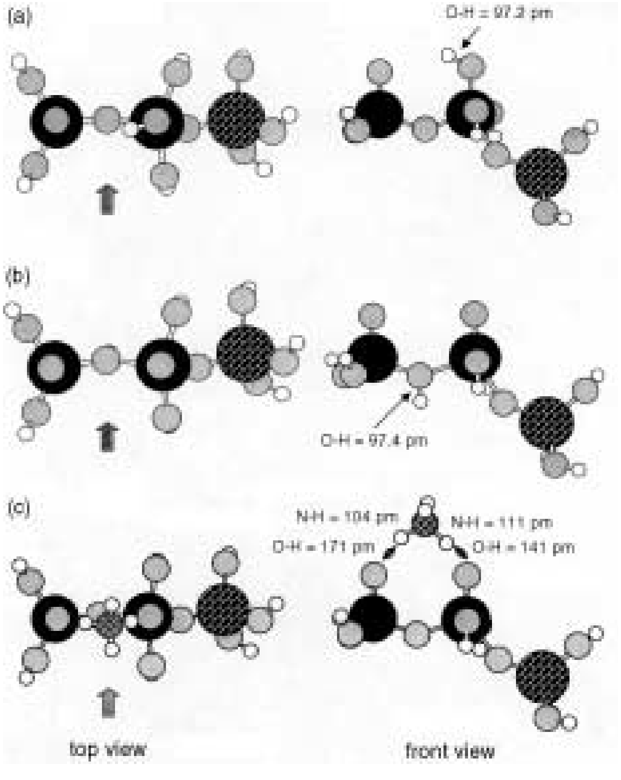


Figure 6. Top and front views of structures of TiV_2 cluster (a) with hydrogen atom transferred to O[1]; (b) with hydrogen atom transferred to O[2]; and (c) upon ammonia adsorption at O[1]. Titanium is colored black and has brick hatching in this and all subsequent figures. Arrows indicate direction of view.

surface of titania (*i.e.*, this moiety was chosen to preserve the formal valence of Ti to be +4), we suggest that this mildly endothermic energy change for the transfer of a hydrogen atom from the $Ti(OH)_4$ moiety to the $V_2O_7H_4$ cluster could be more favorable on the surface of a vanadia/titania catalyst. Accordingly, the TiV_2 cluster appears to give justification for the simple cluster chosen by Gilardoni *et al.* [8], where the $Ti(OH)_3$ group of the TiV_2 cluster is replaced by an H atom.

The interaction of ammonia with a hydrogen atom at the O[1] position of the TiV_2 cluster leads to the formation of NH_4 species, as shown in the structure given in figure 6(c). The corresponding ammonia adsorption energy change is −83 kJ/mol. The O−H bond to the vanadyl group bonded to $Ti(OH)_3$ has a length of 141 pm (with a corresponding N−H bond length of 111 pm), and the O−H bond to the vanadyl group not bonded to $Ti(OH)_3$ has a length of 171 pm (with a corresponding N−H bond length of 104 pm). The difference in bond lengths is likely caused by the asymmetric nature of the TiV_2 cluster. Adding a second $Ti(OH)_4$ group to the second vanadyl group would restore symmetry to the cluster and would likely result in the adsorption of NH_4 with equal O[1]−H bond lengths.

A cluster consisting of four vanadium atoms was also tested, denoted as V_4 and shown in figure 7(a). The V_4 cluster, which has a stoichiometry of $V_4O_{16}H_{12}$, was constructed by taking four vanadium atoms from the (010) plane of V_2O_5, including all oxygen atoms within the plane that are directly bonded to the four vanadium atoms. Hydrogen atoms were then added to maintain charge neutrality. The dihedral angles of the hydrogen atoms were chosen to minimize hydrogen bonding among neighboring −OH groups. One hydrogen atom was transferred from an O[2] position to an O[1] position to produce a VOH adsorption site. The positions of the bridging and terminal OH groups were allowed to fully relax to minimize electronic energy. The positions of the four vanadium atoms were kept fixed, and the four O[1] atoms were free to relax only along the V=O bond.

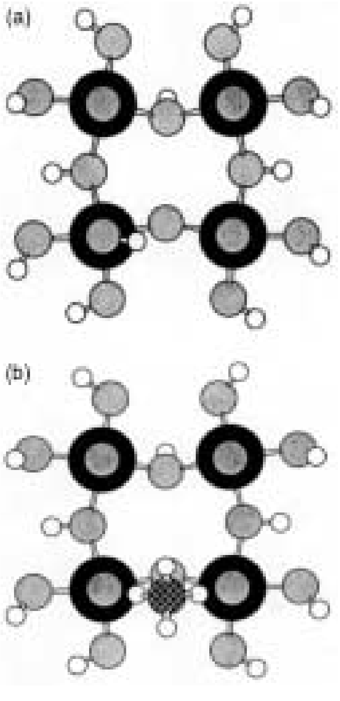


Figure 7. (a) V_4 cluster and (b) V_4 cluster after NH_3 adsorption at O[1].

After optimization of the V_4 cluster, ammonia was subsequently adsorbed onto the cluster. The optimized geometry of ammonia adsorbed at the O[1] position is shown in figure 7(b). During optimization, the bridging and terminal hydroxyl groups were held fixed, as were the positions of the four vanadium atoms. The O[1] atoms were allowed to relax along the V=O bond. The bridging oxygen atom between the V=O and VO[1]−H groups where adsorption takes place was allowed to fully relax, as were the atoms of the NH_3 adsorbed species. The adsorbed ammonia forms a NH_4 species on the V_4 cluster between two V=O sites, which is in agreement with previous experimental results [1–3,5,6] and theoretical calculations [8–10]. The calculated energy of adsorption is −110 kJ/mol, which is in agreement with the reported theoretical calculations [8].

Based on the relative bond strengths of the H atom on the different O sites [25], one would expect VO[2]−H to have the strongest Brønsted acidity; however, our calculations show that the VO[2]−H site is not energetically favorable for the formation of NH_4 species. In particular, interaction of ammonia with a H atom bonded at an O[2] position leads to a H-bonded NH_3 species. It should be noted that the neighboring terminal VOH groups make the O[2]−H hydrogen atom sterically hindered, which could cause adsorption at the O[2]−H site to be difficult.

According to previous experimental results [3–5] the adsorption of ammonia on titanium oxide occurs primarily on Lewis acid sites. To test whether ammonia adsorbs to form NH_4 species on Ti−OH centers adjacent to V=O groups, the V_3Ti cluster shown in figure 8 was constructed, using the optimized V_4 cluster from figure 7(a) as a template. In particular, the V_3Ti cluster was constructed by substituting a Ti atom for one of the V atoms, adding a hydrogen atom to the bridging oxygen atom to balance electronic charge. This V_3Ti cluster was then optimized by relaxing the positions of the terminal and bridging hydroxyl groups associated with the Ti atom. All other hydroxyl groups were held fixed. As in the V_4 cluster, the O[1] atoms were allowed to relax along the V=O or Ti−H bond only, and the positions of the three V atoms and the Ti atom were held fixed.

The optimized geometry of NH_3 adsorbed on the V_3Ti cluster is shown in figure 8(b). In contrast to the V_4 cluster, ammonia adsorbs on the V_3Ti cluster at the Ti−OH group as a H-bonded NH_3 species. The calculated adsorption energy is −65 kJ/mol, which reflects the weaker strength of adsorption for this hydrogen-bonded NH_3 on the

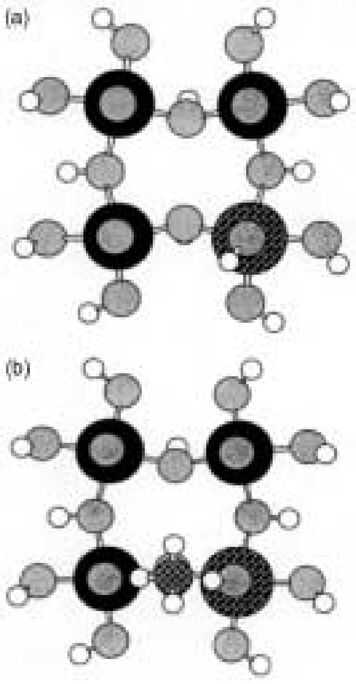


Figure 8. V_3Ti cluster (a) before NH_3 adsorption and (b) after NH_3 adsorption.

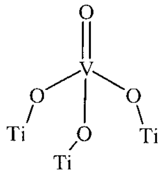
V_3Ti cluster, compared to the formation of NH_4 species on the V_4 cluster.

4. Discussion

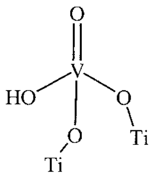
Previous FTIR studies [3] have shown that the surface V–OH structure is sensitive to oxidation/reduction pretreatment of the vanadia/titania catalyst. The concentration of Brønsted acid sites decreases as the catalyst is reduced by treatment in NH_3 at elevated temperatures. In agreement with this experimental observation, our DFT calculations show that the adsorption of ammonia as NH_4 species is preferred on V–OH centers which are fully oxidized. In particular, adsorption of ammonia on the H-$V_2O_7H_4{\cdot}(H_2O)_2$ clusters of figure 2 gave only H-bonded NH_3 species, and one of the V atoms in this cluster has a formal oxidation state of 4+. In contrast, the $V_2O_9H_8$ cluster derived from the $V_2O_7H_4{\cdot}(H_2O)_2$ cluster, the TiV_2 cluster, and the V_4 cluster of the present study, as well as the $V_2O_9H_7$ cluster proposed by Gilardoni *et al.* [8], all have V cations in higher formal oxidation states, and all of these clusters formed NH_4 species upon ammonia adsorption. The role of titania as a support for vanadium oxide may, therefore, be to produce Brønsted acid sites by stabilization of H atoms bonded to vanadium oxide moieties in a fully oxidized state. Furthermore, the results from the present DFT calculations suggest that penta-coordinate vanadia species, rather than tetra-coordinate vanadia species, appear to be most favorable for the formation of NH_4 upon adsorption of NH_3, *i.e.*, penta-coordinate vanadia species favor the formation of Brønsted acid sites. The Brønsted acidity of unsupported V_2O_5 can thus be explained by the fact that each vanadium atom is bonded to five oxygen atoms, that the vanadium atom belonging to the VOH acid site is in an oxidized state (figure 7(a)) and that the hydrogen atom bonds preferentially to V=O.

A second possible role of titania as a support for vanadium oxide may be to stabilize the oxidized vanadium oxide species responsible for the formation of NH_4 species. Full optimization of the clusters shown in figures 4(a) and 5(c) resulted in fragmentation to form monomeric vanadia species. However, when the vanadia clusters were terminated with titania moieties (figure 6(a) and (b)) instead of hydrogen atoms, the vanadia dimers remained intact. One would expect that the clusters shown in figure 6(a) and (b) are better models of the surface vanadia species compared to the H-terminated clusters shown in figures 4(a), 5(a), or 5(c). However, terminating all V–O single bonds with titania moieties is computationally expensive, especially for larger vanadia clusters. Our calculations show that H-terminated vanadia clusters can be used to model titania-terminated clusters, provided that suitable geometric constraints are employed during optimization to ensure that the clusters remain intact.

The results from this study can be used to suggest the following qualitative description of vanadia/titania catalysts. At low loadings of vanadia, monomeric species of VO_4H_3 react with Ti–OH groups to give H_2O and structures such as:

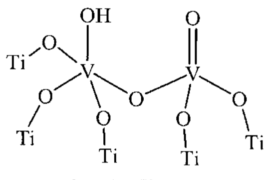


Species Ia

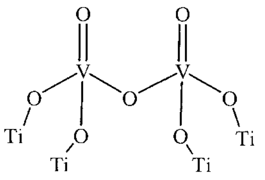


Species Ib

This condensation of VO_4H_3 species with Ti–OH groups leads to a decrease in the number of surface hydroxyl groups. At higher loadings, these monomeric vanadia species form oligomers such as:



Species IIa



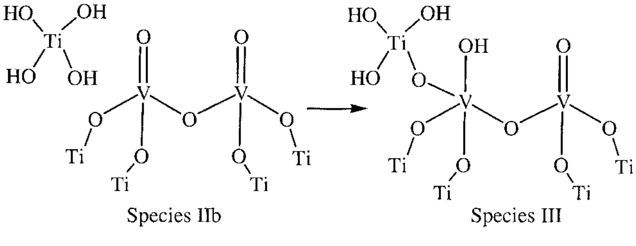
Species IIb

According to the DFT calculations of this study, these oligomerization reactions are energetically rather neutral.

We suggest that one effective route to form Brønsted acid sites on vanadia/titania catalysts is the formation of structures such as Species IIa. Our DFT calculations show that the formation of ammonium species is not energetically favorable upon ammonia interaction with monomeric VO_4H_3 species or with Ti–OH species adjacent to V=O groups. Rather, our results [25] show that bonding of hydrogen atoms is particularly favorable at the O[1] position in the larger clusters found mainly in catalyst with higher vanadia loading. The NH_4 species formed is then stabilized between two V=O groups. This is in agreement with other theoretical results [8–10] reported in the literature, which show that interaction of NH_3 with a V–OH group adjacent to a V=O group leads to formation of ammonium species. Moreover, our DFT calculations show that O[2]–H sites are not Brønsted acid sites in that formation of ammonium species is not energetically favorable at this position and NH_4 species is not stabilized between O[2] and O[1].

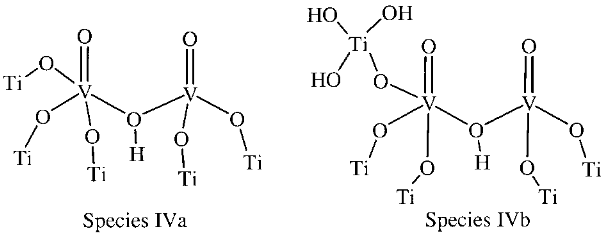
It is noteworthy that the present findings are consistent with the literature regarding the formation of NH_4 species on Brønsted acid sites in zeolites. When ammonia interacts solely with an –OH group, it forms hydrogen-bonded NH_3, in contrast to the formation of NH_4 species. The formation of NH_4 species is facilitated by the multiple coordination of these species with at least two oxygen atoms from the zeolite, *i.e.*, forming multidentate species. These multidentate NH_4 species may be coordinated to two or more oxygen atoms belonging to the same aluminum atom [11,12,14–17], as believed to be the case for faujasite [14,15] and ZSM-5 [16,17], to a pair of oxygen atoms bonded to a common silicon atom, as believed to be the case for mordenite [17], or to multiple aluminum and silicon atoms in the case of MFI [17] and chabazite [16]. The formation of NH_4 species on vanadia monomers and on vanadia oligomers between oxygen atoms belonging to the same vanadium atom appears to be hindered by electrostatic repulsion between the NH_4 cation and the high-valent vanadium cation. Accordingly, NH_4 species are formed preferentially on vanadium oxide clusters between two O[1] sites belonging to adjacent vanadium cations. The possibility that NH_4 might adsorb between two O[2] atoms belonging to adjacent vanadium cations was not investigated, since adsorption in such a manner appears to suffer steric hindrance from V=O[1] groups.

Another possible route to the formation of a Brønsted acid site is the transfer of a hydrogen atom from a Ti–OH group to a vanadium oxide moiety such as Species IIb, as suggested from our DFT calculations. This process is shown schematically below:



Our DFT calculations show that interaction of ammonia with the VO[1]–H in the above TiV_2 cluster leads to formation of ammonium species.

As reported elsewhere [4,5], the number of sites capable of forming ammonium ions upon exposure to ammonia at room temperature is roughly proportional to the vanadia loading, but starts to deviate at higher temperatures of SCR conditions, where significantly more ammonium ions are formed in the higher loading catalysts. Specifically, at higher temperatures, catalysts containing low loadings of vanadia on titania show primarily Lewis acid sites associated with the titania support, whereas Brønsted acid sites are formed preferentially at higher vanadia loadings on titania. These observations could well reflect the important role of hydrogen mobility at elevated temperatures [25], since the surface dynamic behavior is seen predominantly in higher loading catalysts with relatively more vanadia in the polymeric structure. At higher temperatures, hydrogen atoms become mobile on the vanadia–titania catalysts, and they populate the energetically less-favorable bridging oxygen positions, leading to such structures as:



The formation of these structures leads to a decrease in the intensity of the terminal OH band and a shift to lower frequency due to bridged VO–H species, as well as an increase in the number V=O groups. The activation energy barrier calculated in the present study and in our previous work [25] for transfer of a hydrogen atom from O[1] to O[2] leads to a rate constant of *ca.* 1 min^{-1} at 473 K, indicating that this hydrogen transfer is very feasible at the experimental conditions of the present study. In contrast, for catalyst at lower vanadia loadings, the hydrogen atoms appear to be primarily associated with the titania support, such that ammonium species are not favored. Furthermore, mobility of hydrogen does not occur in the lower loading catalysts where predominantly monomeric vanadia structures are present.

Conclusions

Vanadium oxide species formed at low loadings are not as effective at forming Brønsted acid sites as are those species formed at higher loadings. We suggest that Brønsted acid sites may be formed on vanadia/titania catalysts by the interaction of oligomeric vanadium oxide species with the titania support. These oligomeric vanadium oxide species contain V–OH as well as V=O groups, and they are particularly effective for the formation of Brønsted acid sites. In addition, Brønsted acid sites may be formed by the transfer of hydrogen atoms from Ti–OH groups to fully oxidized vanadium oxide moieties. Adsorption of ammonia as NH_4 species occurs between two neighboring V=O[1] groups. In contrast, formation of NH_4 species was not observed on vanadia monomers or on V–O[2]–V groups. Furthermore, the formation of NH_4 species appears to be favored on Brønsted acid sites where the vanadium atom is in an oxidized state. In particular, acid sites in which vanadium was in a reduced (*i.e.*, +4 formal valence) state resulted in the adsorption of ammonia to form hydrogen-bonded NH_3 species.

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