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Density functional theory studies of mechanistic aspects of the SCR reaction on vanadium oxide catalysts

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Abstract

Density functional theory (DFT) calculations were carried out on a vanadium oxide cluster containing four vanadium atoms to probe the mechanism of the selective catalytic reduction (SCR) of NO with ammonia. The interaction of ammonia with Brønsted acid sites on this V_4-cluster leads to the formation of NH_4 species bonded to two vanadyl (V=O) groups, with a bonding energy of -110 kJ/mol. This adsorbed NH_4 species reacts with NO in a series of steps to form an adsorbed NH_2NO species, which subsequently undergoes decomposition to form N_2, H_2O, and a reduced vanadium oxide cluster (V_4–H). The latter reaction occurs via a series of hydrogen-transfer steps by a "push–pull" mechanism with adjacent V=O and V–OH groups on the vanadium oxide cluster. The rate limiting process in this conversion of NO and NH_3 to give N_2, H_2O, and V_4–H involves the reaction of an adsorbed NH_3NHO adduct to form NH_2NO species. The transition state of this step may be stabilized through hydrogen bonding with surrounding vanadia and/or titania moieties.

Keywords: Vanadia; SCR; Ammonia; NO_x; DFT; Reaction mechanism; Hydrogen transfer

1. Introduction

The removal of NO_x from flue gas emitted by power plants remains a major environmental issue today. Despite significant developments in alternative NO_x removal technologies and catalysts, the most widely used process today is the selective catalytic reduction (SCR) of nitric oxide by ammonia over vanadia/titania-based catalysts. In recent years, experimental [1–18] and theoretical [18–31] investigations have been carried out to understand the structural aspects of the catalyst, the nature of the active sites, and the reaction mechanism. For example, in our previous work [18,30], we investigated the state of VO_x surface groups [18] and the nature of the Brønsted acid sites [30] responsible for ammonia adsorption as NH_4 species. There is broad agreement [1,5, 7–9,11–14] that ammonia adsorbs as NH_3 species on Lewis acid sites of titanium oxide and as NH_4 species on Brønsted acid sites associated with vanadium oxide moieties. In contrast, the interaction of NO with the surface of vanadium oxide is believed to be quite weak [1,2,4,7,8,11–13].

Various researchers have proposed that the SCR reaction may take place by reaction of NO with NH_4 species on vanadia/titania catalysts [1,7–14]. Based on experimental observations [8–14], we have proposed previously that the reaction is initiated by adsorption of ammonia on Brønsted acid sites (V–OH), followed by activation of ammonia via reaction with redox sites (V=O). This activated form of ammonia then reacts with weakly adsorbed NO, producing N_2 and H_2O and leading to partial reduction of the catalyst, which is then oxidized by O_2. However, the detailed nature of the steps involved in the reaction of NO with adsorbed NH_4 species is still unclear. Gilardoni et al. [25,26] proposed in a theoretical study that adsorbed NH_4 species react with NO on the surface of vanadium oxide to give a NH_2NO species, which may then isomerize in the gas phase to give N_2 and H_2O. Kobayashi et al. [31] proposed several species derived from NH_2NO as reaction intermediates in a theoretical study of the gas-phase reaction of NH_3 and NH_4 species with NO. In the present study, we have used density functional theory (DFT) to obtain further insight into the mechanism of the SCR reaction, focusing especially on the role of vanadium oxide in the reaction of adsorbed NH_4 species with NO.

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2. DFT calculation methods

Electronic structure calculations employing density functional theory were conducted to probe the energetics of the reaction of NH_3 with NO over a vanadium oxide cluster containing four vanadium atoms. The vanadium oxide cluster used in this study, hereafter referred to as V_4, was used by us previously to probe the factors controlling the nature of ammonia adsorption on surface vanadia species [30]. The V_4 cluster was constructed from the crystal structure of V_2O_5 [32] by selecting adjacent vanadium atoms and all oxygen atoms bonded directly to these vanadium cations. Hydrogen atoms were added to maintain charge neutrality.

The DFT calculations were carried out using DEC workstations with the Jaguar software package (Schrödinger, Inc.). The chosen DFT method uses a hybrid method employing Becke's three-parameters approach, B3LYP [33]. This functional combines the exact HF exchange, Slater's local exchange functional, and Becke's 1988 nonlocal gradient correction to the exchange functional, with the correlation functionals of Vosko, Wilk, and Nusair (VWN) and Lee, Yang, and Parr (LYP). The basis set employed in all calculations (LACVP**) uses an effective core potential on all V atoms, developed at Los Alamos National Laboratory by Hay and Wadt [34]. The electrons treated explicitly on V are the outermost core and valence electrons ($3s^22p^64s^23d^3$). The H, N, and O atoms have been treated with the 6-31G** basis set, with all electrons being treated explicitly.

The energy of each adsorbed species and transition state was calculated relative to the following reaction:

$$V_4 + NH_3(g) + NO(g) \rightarrow V_4\text{-[species]}.$$

Accordingly, we calculate the energy change of each reaction, ΔE, from the terms

$$\Delta E = (E_{V_4\text{-species}}) - (E_{V_4} + E_{NH_3} + E_{NO}),$$

where $E_{V_4\text{-species}}$ is the energy of the V_4 cluster with the species of interest adsorbed, E_{V_4} is the energy of the initial V_4 cluster, and E_{NH_3} and E_{NO} represent the energies of gas-phase NH_3 and NO, respectively.

3. Results

3.1. Formation of NH_2NO from NH_3 and NO

It has been proposed in the literature [17,25,26] that the NH_2NO species is a possible intermediate in the reaction of NO with ammonia over vanadium oxide catalysts. Accordingly, we will first consider the steps involved in the formation of adsorbed NH_2NO on the vanadia cluster. We will then address the steps involved in the catalytic decomposition of NH_2NO to form N_2 and H_2O.

The cluster used to model the reaction of NH_3 with NO over a V_2O_5 catalyst is shown in Fig. 1a. This cluster, denoted V_4, is described elsewhere [30]. In short, 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. Oxygen atoms in this cluster are coordinated to either 1 or 2 vanadium atoms, as denoted by O[1] or O[2], respectively. Hydrogen atoms were then added to oxygen atoms 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. According to the literature [19], as well as our previous calculations [18], O[1] atoms are stronger hydrogen acceptors than O[2] atoms, thus making the transfer of a hydrogen atom from O[2] to O[1] exothermic. The positions of the bridging and terminal OH groups were allowed to relax fully 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. The V=O bond length in the V_4 cluster is 157 pm, which is in agreement with the crystal structure obtained by Byström et al. [32].

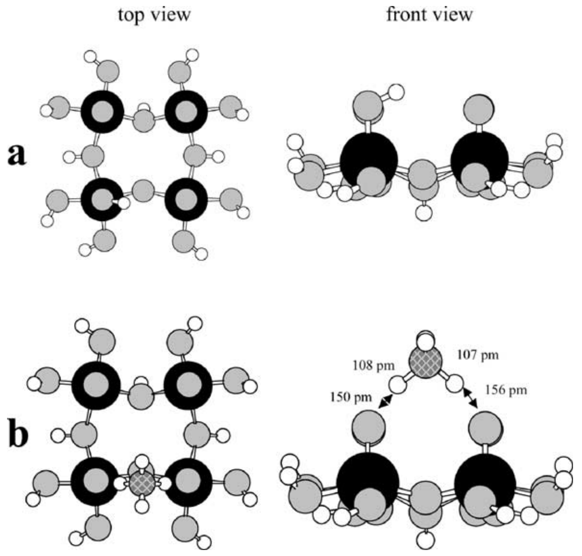

Fig. 1. Top and front view of (a) V_4 cluster, (b) V_4 cluster with adsorbed NH_4. The following coloration is used in this and all subsequent figures: H—white, O—gray, N—gray with crosshatching, V—black.

After optimization of the V_4 cluster in the manner described above, the cluster was reoptimized to allow relaxation of the four vanadium atoms. The V–V distances in the cluster subsequently increased slightly from values of 341 and 357 pm to values of 346 and 361 pm. The energy of the V_4 cluster decreased by 11 kJ/mol during relaxation. Because the V–V distances changed only slightly during optimization, all subsequent calculations were performed with the V–V distances constrained at 341 and 357 pm.

The optimized V_4-cluster was then used to study ammonia adsorption. The optimized V_4–NH_3 geometry is shown in Fig. 1b. During optimization of the V_4–NH_3 geometry,

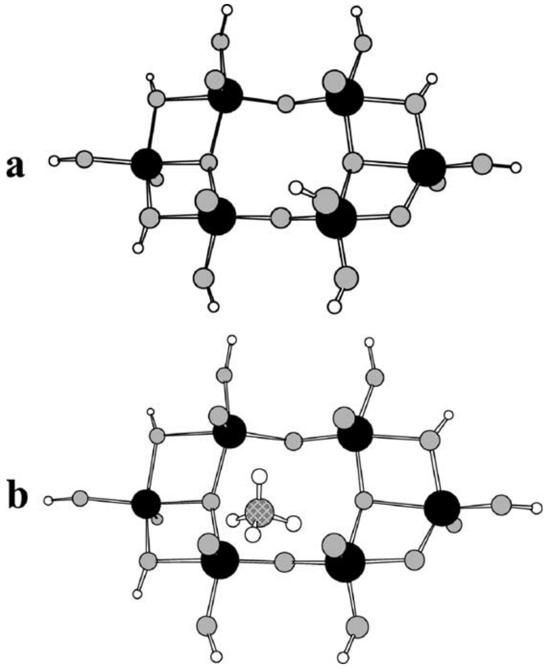

Fig. 2. (a) V_6 cluster; (b) NH_3 adsorbed on O[1]–H group of V_6 cluster.

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 only along the V=O bond. The bridging O atom between the two V=O groups involved in ammonia adsorption was allowed to relax fully, as were the atoms of the NH_4 adsorbed species. Ammonia adsorbs as an NH_4 species on the V_4 cluster between two V=O sites, which is in agreement with previous experimental results [1,5,7–9,11–14] and theoretical calculations [25, 26,30]. Adsorption of ammonia is symmetric: the two N–H bond lengths are 108 and 107 pm, with corresponding VO–H bond lengths of 150 and 156 pm, respectively. The calculated energy change of adsorption is −110 kJ/mol, which is in agreement with the theoretical calculations of Gilardoni et al. [25,26]. In a previous paper [30], we showed that the formation of NH_4 species is facilitated on oligomeric clusters of vanadium oxide containing pentacoordinated vanadium cations, and these species are promoted by interaction of vanadium oxide with the titanium oxide support. Also, to investigate the effect of cluster size while maintaining the vanadium atom of the VOH in an oxidized state, a V_6 cluster was constructed, as shown in Fig. 2a. On this cluster, ammonia was found to adsorb as NH_4 species, as shown in Fig. 2b, with a heat of adsorption of −132 kJ/mol. Thus, the effect of cluster size on the energy change of ammonia adsorption appears to be rather small.

The V_4 cluster was also used to investigate the adsorption of ammonia on O[2]–H sites. The structure of ammonia adsorbed on an O[2]–H group is shown in Fig. 3. Ammonia adsorbs as NH_3 species on O[2]–H groups, with a heat of adsorption of −53 kJ/mol. This result agrees with our previously reported work [30], in which it was found that the adsorption of NH_3 as NH_4 species does not take place on O[2]–H groups. As shown in Fig. 4, adsorption of ammonia on O[3]–H groups of the V_6 cluster was also investigated. Ammonia adsorbs on O[3]–H groups as a distorted NH_4 species: the H_3N–H bond length is 119, and the NH_4–O[3] bond length is 130 pm. This NH_4 species adsorbs with a heat of −101 kJ/mol. Because of the stronger interaction of ammonia with O[1]–H sites compared to O[3]–H sites, we

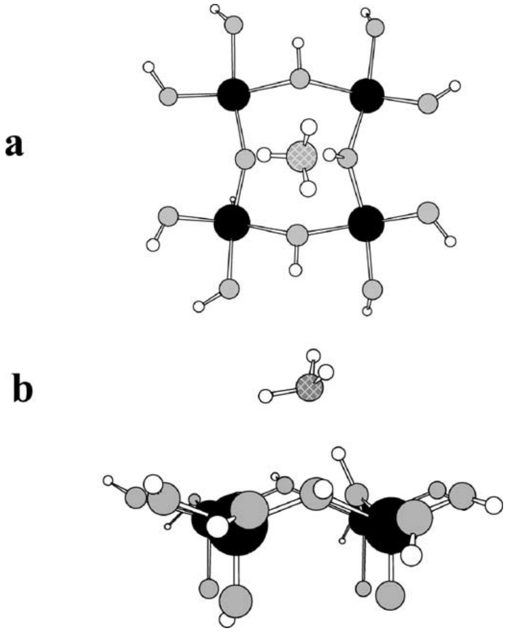

Fig. 3. (a) Top and (b) front views of ammonia adsorbed as NH_3 on O[2]–H group of V_4 cluster.

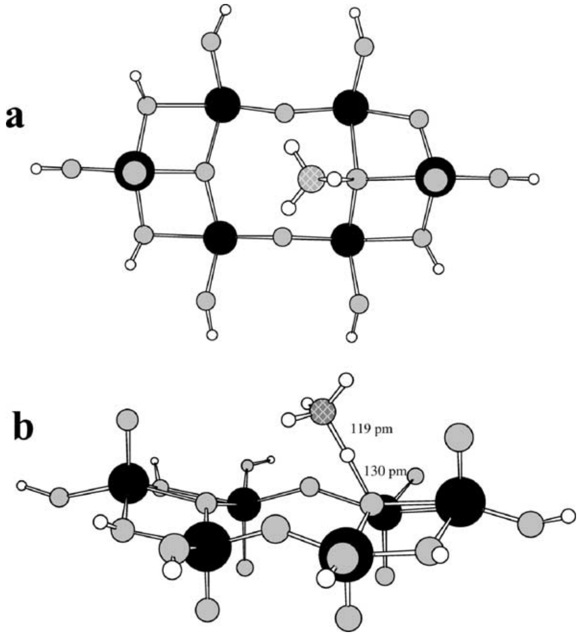

Fig. 4. (a) Top and (b) front views of ammonia adsorbed on O[3]–H group of V_6 cluster.

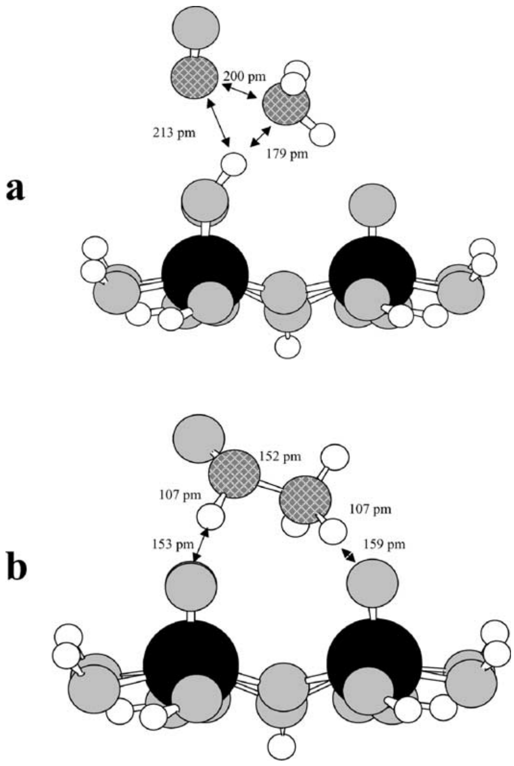

Fig. 5. (a) Approximate transition state in the reaction of NO with NH_4 species, and (b) the NH_3NHO species formed in this reaction.

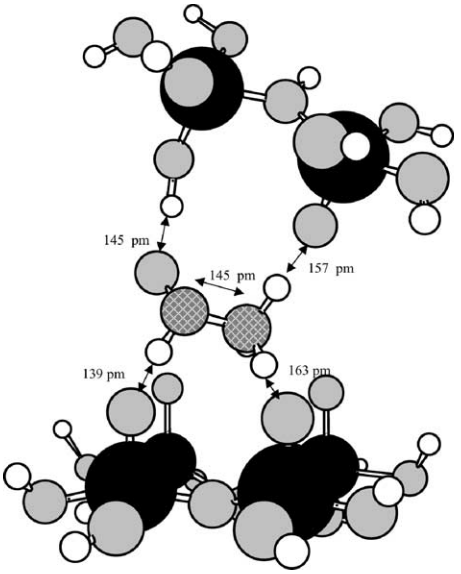

Fig. 6. NH_3NHO adsorbed species associated with V_4 and V_2 clusters.

have focused our attention on the former sites to probe the reaction of NO with adsorbed NH_4 species.

Adsorption of NO on the V_4 cluster was studied. Two cases were attempted: one case with the N atom oriented toward the VOH group, and a second geometry with the O atom oriented toward the VOH group. In neither case did NO interact significantly with the Brønsted acid site. Thus, our calculations agree with experimental results [1,2,6–8, 11–14], which indicate that the selective catalytic reduction of NO by ammonia takes place between an adsorbed ammonia species and gas-phase or weakly adsorbed NO.

The first intermediate species formed by reaction of NO with adsorbed NH_4 species is adsorbed NH_3NHO. The transition state for the formation of this species and the optimized geometry of this adsorbed NH_3NHO species are shown in Figs. 5a and 5b. The approximate transition state was obtained by selecting the maximum energy point in a series of optimized geometries where the N–N bond was constrained and all other atoms in the NH_4–NO complex were relaxed fully. The cluster was optimized in the same fashion as the V_4–NH_3 cluster shown in Fig. 1b. At the approximate transition state, three bonds are in the process of being formed or broken: the N–N bond, which has a length of 200 pm, the H–NO bond, which has a length of 213 pm, and the H–NH_3 bond, which has a length of 179 pm. The energy of the transition state with respect to the V_4 cluster and gas-phase NH_3 and NO is $+4$ kJ/mol. The adsorbed NH_3NHO adduct formed in this reaction has an N–N bond length of 152 pm and an energy of -25 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO, which is similar to the geometry and structure of the NH_3NHO adduct postulated by Kobayashi et al. [31].

We have also considered another situation where the NH_3NHO adduct is formed between two vanadia moieties, as shown in Fig. 6. In this configuration, the NH_3NHO adduct interacts with the V_4 cluster (Fig. 1a) and a V_2 cluster obtained from the V_4 cluster as follows. Two vanadium atoms were removed from the V_4 cluster, along with their associated V=O and V–OH groups. The resulting dangling V–O bonds were terminated with hydrogen atoms. In order to maintain the two vanadium atoms at the same oxidation state as the vanadium atoms in the V_4 cluster, a hydrogen atom was bonded at the bridging oxygen atom of the V_2 cluster. The V_2 cluster was optimized under the same constraints as the V_4 cluster. During geometry optimization, the atoms of the NH_3NHO adduct were allowed to relax fully, and the orientation of the V_2 cluster with respect to the V_4 cluster was unconstrained. Upon optimization of the V_4–NH_3NHO–V_2 ensemble, two new hydrogen bonds were formed: a NH–OV bond between the –NH_3 end of the adduct and the V_2 cluster (157 pm), and a shorter NO–HOV bond between the –NO end of the adduct and the V_2 cluster (145 pm). In addition, the existing NOH–OV bond between the –NO end of the adduct and the V_4 cluster shortened from 153 to 139 pm, and the N–N bond contracted from 152 to 145 pm. The existing NH–OV bond between the –NH_3 end of the adduct and the V_4 cluster lengthened slightly from 159 to 163 pm. Upon the forming of two new hydrogen bonds, the energy of the NH_3NHO adduct was lowered by 67 kJ/mol to a value of -92 kJ/mol with respect to gas-phase NH_3 and NO. For comparison with this stabilization effect of the V_2 cluster, we have also considered the case where V_4–NH_3NHO adduct is stabilized by interaction with a Ti_2 cluster having a $Ti_2O_7H_6$ stoichiometry, as shown in

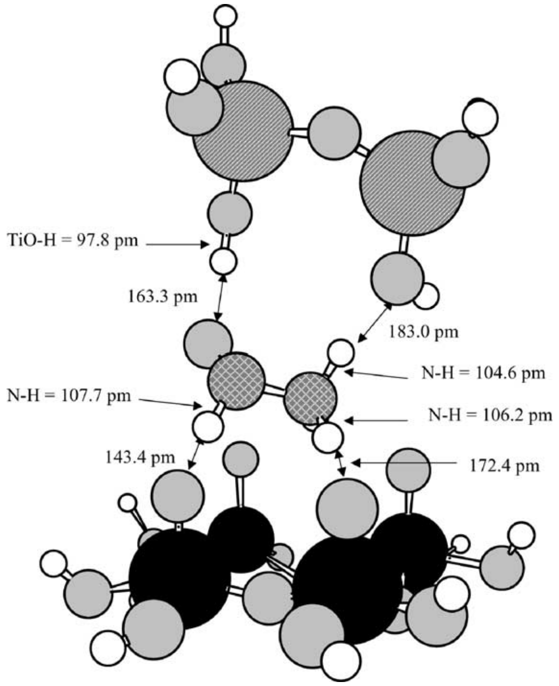

Fig. 7. NH_3NHO adsorbed species associated with V_4 and Ti_2 clusters. Ti atoms are shown in gray with diagonal hatching.

Fig. 7. The energy of the V_4–NH_3NHO adduct was lowered upon interaction with the Ti_2 cluster by 33 kJ/mol to a value of −58 kJ/mol with respect to gas-phase NH_3 and NO.

The adsorbed NH_3NHO adduct forms an NH_2NO species by transferring two hydrogen atoms to the V_4 cluster, as shown in Fig. 8. The approximate transition state for the conversion of NH_3NHO to NH_2NO is shown in Fig. 8a. At the approximate transition state, the first hydrogen atom has been removed to form a NH_2NHO species. The N–H bond length on the hydrogen atom being transferred is 135 pm; the corresponding VO–H bond length is 125 pm. The hydrogen atom belonging to the –NHO group, however, has yet to begin transfer: the VO–H bond length is 163 pm, with a corresponding N–H bond length of 105 pm. The energy of the transition state is +48 kJ/mol with respect to the V_4 cluster and gas-phase NO and NH_3. The NH_2NO reaction product is shown in Fig. 8b. This NH_2NO species adsorbs onto the V_4-cluster through a hydrogen bond (166 pm) between VOH and the nitrogen atom of the –NO portion of the NH_2NO molecule. The energy of the adsorbed NH_2NO species on the V_4–H cluster is −87 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO. The energy of the V_4–H cluster plus gas-phase NH_2NO is −42 kJ/mol relative to the V_4 cluster plus gas phase NO and NH_3.

In summary, we have found that gas-phase NH_2NO may be formed via the following set of reactions:

$$NH_3(g) + V{=}O + VOH \rightarrow (V{=}O)\text{–}NH_4\text{–}(O{=}V),$$

$$(V{=}O)\text{–}NH_4\text{–}(O{=}V) + NO(g)$$

$$\rightarrow (V{=}O)\text{–}NH_3NHO\text{–}(O{=}V),$$

$$(V{=}O)\text{–}NH_3NHO\text{–}(O{=}V) \rightarrow (VOH)\text{–}NH_2NO + VOH,$$

$$(VOH)\text{–}NH_2NO \rightarrow VOH + NH_2NO(g).$$

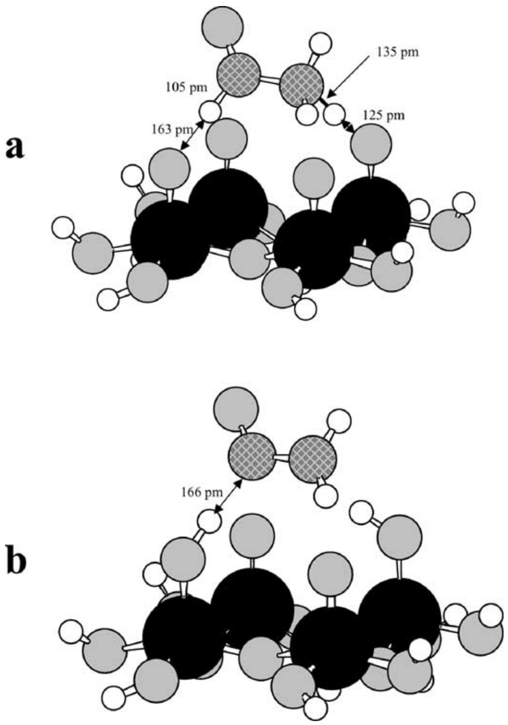

Fig. 8. (a) Approximate transition state in the reaction of NH_3NHO and (b) the NH_2NO species formed in this reaction.

3.2. *Decomposition of NH_2NO*

The results from our DFT calculations show that to form N_2 and H_2O, the NH_2NO reaction intermediate formed above must undergo a series of hydrogen-transfer steps in a “push–pull” manner on the vanadia cluster. In each of these steps, a hydrogen atom is transferred from a VOH group to an adsorbed species with NH_2NO stoichiometry, and a second hydrogen atom is simultaneously transferred from the NH_2NO-stoichiometric species to an adjacent V=O group. Our reaction mechanism resembles the mechanism for the dehydrogenation of propane over vanadium oxide reported by Gilardoni et al. [27], in which hydrogen atoms from propane are shuttled among neighboring O[1] and O[3] atoms during the course of reaction. For simplicity, we use a V_4-cluster to accomplish these hydrogen-transfer steps, in contrast to using a V_4–H cluster. (In particular, the V_4-cluster does not have unpaired electrons, and the DFT computational time for this cluster is half the time required for calculations involving the V_4–H cluster, which has an odd number of electrons.) The various NH_2NO-stoichiometric species formed during the isomerization and decomposition of the NH_2NO are shown and named in Fig. 9.

The first step toward the decomposition of NH_2NO is the surface-catalyzed isomerization of NH_2NO to form *trans*-HN=NOH, as shown in Fig. 10. The energy of NH_2NO adsorbed on the V_4 cluster, shown in Fig. 10a, is −92 kJ/mol

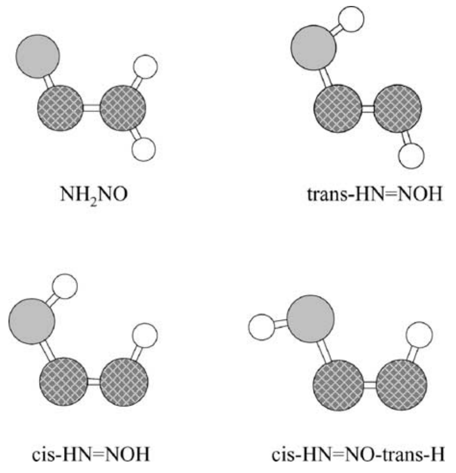

Fig. 9. Intermediate species involved in the isomerization and decomposition of NH_2NO.

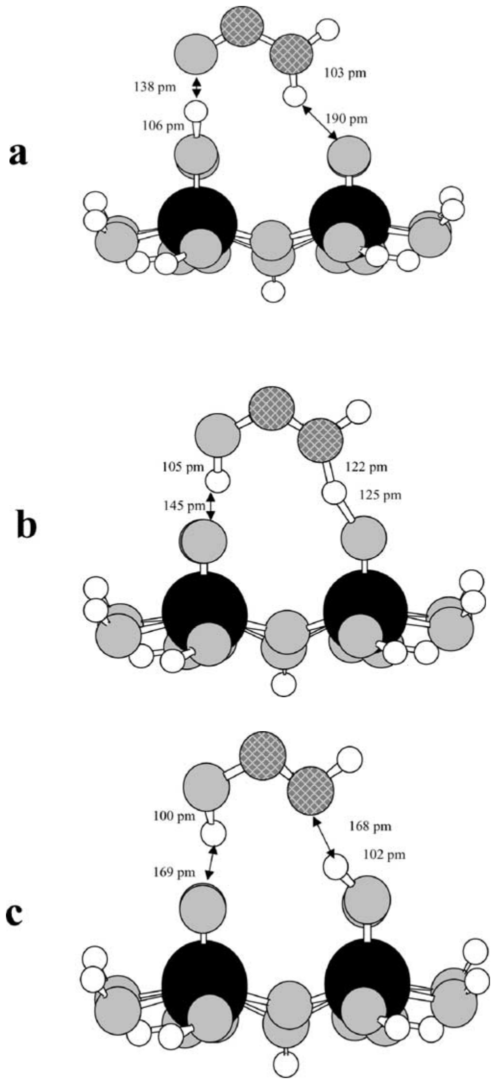

Fig. 10. (a) NH_2NO species adsorbed on V_4 cluster; (b) approximate transition state in the reaction of NH_2NO to form *trans*-HN=NOH; (c) adsorbed *trans*-HN=NOH species.

with respect to the V_4 cluster and gas-phase NH_3 and NO, or −50 kJ/mol with respect to the V_4 cluster and gas-phase NH_2NO. An approximate transition state for the isomerization of NH_2NO to form adsorbed *trans*-HN=NOH was obtained by selecting the maximum energy point in a series of constrained geometry optimizations, where the NH–O bond was constrained at successively shorter distances and the remaining atoms of the NH_2NO adduct were allowed to relax fully. The approximate transition state, shown in Fig. 10b, has an energy of −73 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO. At the approximate transition state, the hydrogen atom of the –NH_2 group is equally shared by the adduct and the V_4-cluster; i.e., the N–H and VO–H bond lengths are 122 and 125 pm, respectively. The hydrogen atom being transferred to the –NO group, however, has been almost completely transferred to the adduct, i.e., the NO–H and VO–H bond lengths are 105 and 145 pm, respectively. The final reaction product, adsorbed *trans*-HN=NOH, is shown in Fig. 10c. A "push-pull" mechanism appropriately describes how the hydrogen atom is transferred from the VO–H group on the vanadia surface to the –NO group of the adsorbed NH_2NO, while the hydrogen atom of the –NH_2 of the adsorbed intermediate is transferred to the V=O group of the vanadia. The adsorbed *trans*-HN=NOH species has an energy of −82 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO.

The *trans*-HN=NOH formed on the surface must then isomerize to form *cis*-HN=NOH as shown in Fig. 11. This isomerization step involves adding and removing a hydrogen atom from the same nitrogen atom. The energy of the adsorbed *trans*-HN=NOH species upon readsorption in the fashion shown in Fig. 11a is −72 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO. An approximate transition state, shown in Fig. 11b, for the isomerization reaction to form *cis*-HN=NOH was obtained by selecting the maximum energy point in a series of constrained geometry optimizations, where the VO–H bond which is broken during isomerization reaction was constrained at successively longer lengths and the remaining atoms of the NH_2NO species were allowed to relax fully. In the approximate transition state, one of the nitrogen atoms is partially bonded to two hydrogen atoms, with N–H bond lengths of 112 and 107 pm respectively, and with corresponding VO–H bond lengths of 139 and 160 pm. The energy of the transition state is −50 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO. The adsorbed *cis*-HN=NOH reaction product is shown in Fig. 11c, and it has an energy of −53 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO.

Before the adsorbed *cis*-HN=NOH species can react further to form N_2 and H_2O, the DFT calculations show that an isomerization step must first take place to form the *cis*-HN=NO-*trans*-H species shown in Fig. 12, which presents an energetically more favorable orientation for the decomposition reaction. The approximate transition state for this isomerization reaction, shown in Fig. 12a, was obtained

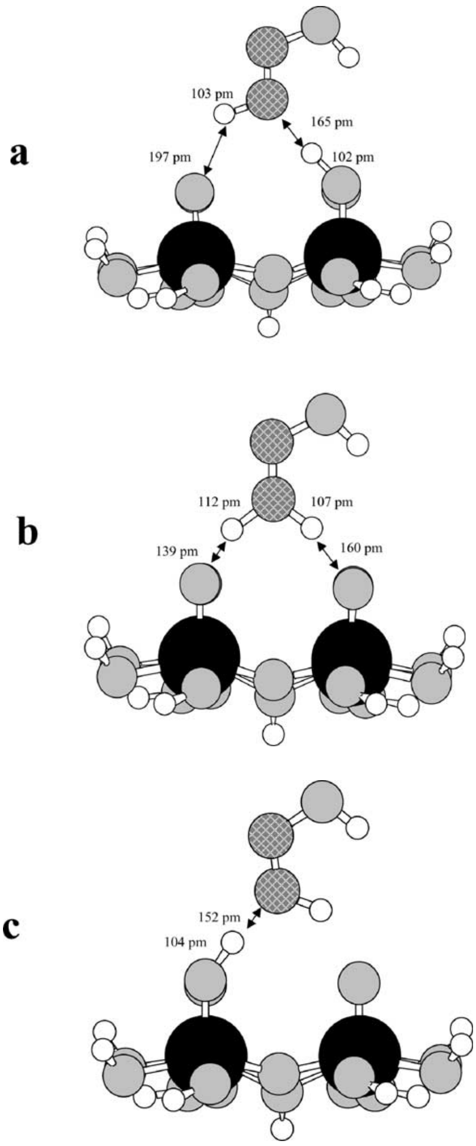

Fig. 11. (a) *trans*-HN=NOH species readsorbed on V$_4$ cluster; (b) approximate transition state in the reaction of the *trans*-HN=NOH to form *cis*-HN=NOH reaction, (c) adsorbed *cis*-HN=NOH species.

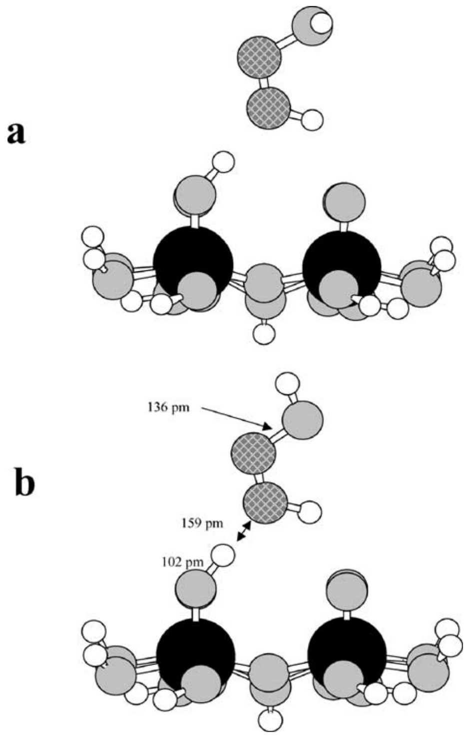

Fig. 12. (a) Approximate transition state in the reaction of the *cis*-HN=NOH to form *cis*-HN=NO–*trans*-H; (b) adsorbed *cis*-HN=NO–*trans*-H species.

by fixing the dihedral angle of the rotating hydrogen atom to a position halfway between the two isomers. The energy of the transition state was found to be -28 kJ/mol with respect to the V$_4$ cluster and gas-phase NH$_3$ and NO. The adsorbed *cis*-HN=NO-*trans*-H reaction product is shown in Fig. 12b, and it has an energy of -76 kJ/mol with respect to the V$_4$ cluster and gas-phase NH$_3$ and NO.

The formation of N$_2$ and H$_2$O takes place via the hydrogen-assisted decomposition of adsorbed cis-HN=NO-*trans*-H, as shown in Fig. 13. The energy of adsorbed *cis*-HN=NO-*trans*-H upon readsorption as shown in Fig. 13a is -61 kJ/mol with respect to the V$_4$ cluster and gas-phase NH$_3$ and NO. The N–O bond distance of *cis*-HN=NO-*trans*-H adsorbed as in Fig. 12b is 136 pm, whereas the N–O bond lengthens to 150 pm in the geometry of Fig. 13a. The length of the O–H bond between the oxygen atom of *cis*-HN=NO–*trans*-H and the VOH group is correspondingly short, at 153 pm. An approximate transition state, shown in Fig. 13b, was determined by selecting the maximum energy point in a series of constrained geometry optimizations, where the

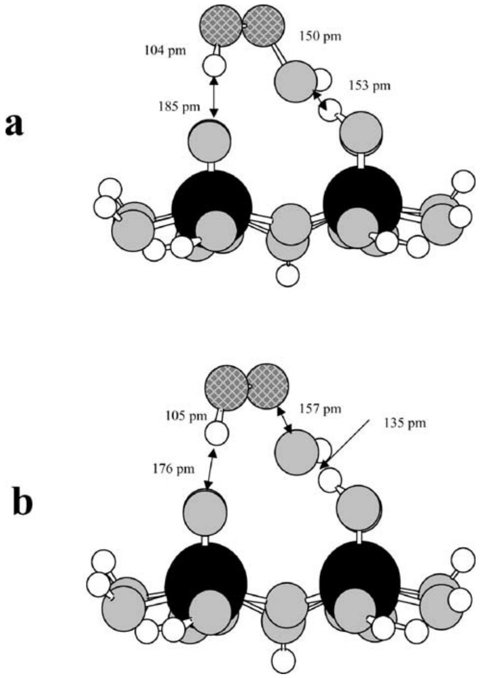

Fig. 13. (a) Readsorbed *cis*-HN=NO–*trans*-H species; (b) approximate transition state in the reaction of *cis*-HN=NO–*trans*-H to form N$_2$ and H$_2$O.

Table 1
Comparison of energies of intermediate species (with respect to the V_4 cluster and gas-phase NH_3 and NO) adsorbed on V_4 singlet and doublet clusters

Species	Energy w.r.t. V_4 (singlet), NH_3(g), NO(g), kJ/mol	Energy w.r.t. V_4 (doublet), NH_3(g), NO(g), kJ/mol
V_4–NH_2NO	−92	−94
V_4–*trans*-HN=NOH	−82	−79
V_4–*cis*-HN=NOH	−53	−55
V_4–*cis*-HN=NO-*trans*-H	−76	−73

length of the bond between the O atom of the HN=NOH species and the H atom of the VOH surface group was constrained at successively shorter bond lengths, and the remaining atoms of the HN=NOH species were allowed to relax fully. The approximate transition state occurs at an O–H bond length of 135 pm, and it has an energy of −57 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO. The energy of the N_2 and H_2O formed is −273 kJ/mol with respect to the V_4 cluster and gas-phase NH_3 and NO.

To test the possible effect of the cluster spin-state on the reaction chemistry for catalyst-assisted decomposition of NH_2NO, the four intermediate species with stoichiometry NH_2NO (i.e., NH_2NO, *trans*-HN=NOH, *cis*-HN=NOH, and *cis*-NH=NO–*trans*-H) were optimized over a doublet V_4 cluster, formed by adding a H atom at an O[2] position. The energies of these adsorbed species for the singlet and doublet V_4 clusters are compared in Table 1. For all adsorbed species, the difference in energy between the species adsorbed on a singlet V_4 cluster and a doublet V_4 cluster is only 2–3 kJ/mol. Therefore, it is expected that the decomposition of NH_2NO between neighboring O[1]–H and V=O groups should take place regardless of whether an unpaired electron is present in the local environment.

The possibility that NH_2NO species may decompose via a series of hydrogen transfer reactions involving O[2]–H groups was also investigated. The transition state energies for each step were approximated by superimposing the transition state geometry for each step, as shown in Figs. 10b, 11b, 12a, and 13b, on the underside of the V_4 cluster. The approximate transition state for the NH_2NO → *trans*-HN=NOH reaction is shown in Fig. 14 as an example. The energies of the first two transition states (analogous to Figs. 10b and 11b) increase by approximately 40 and 65 kJ/mol, respectively, compared to reactions involving O[1]–H groups. This increase in energy may be due to steric factors, since rotation of hydrogen atoms bonded to O[2] atoms is more restricted compared to hydrogen atoms bonded to O[1] atoms. Thus, it is expected that O[1]–H and V=O species play the dominant role in the decomposition of NH_2NO to N_2 and H_2O.

The above results for the decomposition of the NH_2NO intermediate (formed in the previous section) over the vanadium oxide via a series of hydrogen-transfer reactions are summarized in the following reaction mechanism:

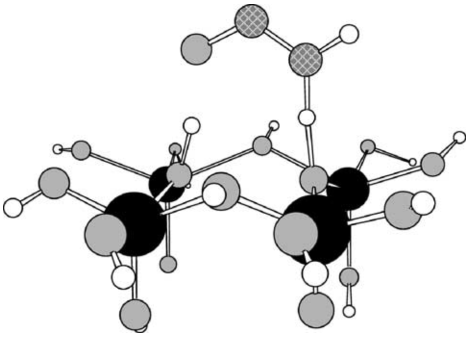

Fig. 14. Transition state for NH_2NO → *trans*-HN=NOH over O[2]–H groups.

$$
\begin{aligned}
&NH_2NO(g) + VOH \rightarrow NH_2NO\text{–}(VOH),\\
&NH_2NO\text{–}(VOH) + V{=}O\\
&\quad \rightarrow (VOH)\text{–}\textit{trans}\text{–}HN{=}NOH + V{=}O,\\
&(VOH)\text{–}\textit{trans}\text{-}HN{=}NOH + V{=}O\\
&\quad \rightarrow (VOH)\text{–}\textit{cis}\text{-}HN{=}NOH + V{=}O,\\
&(VOH)\text{–}\textit{cis}\text{-}HN{=}NOH \rightarrow (VOH)\text{–}\textit{cis}\text{-}HN{=}NO\text{–}\textit{trans}\text{-}H\\
&(VOH)\text{–}\textit{cis}\text{-}HN{=}NO\text{–}\textit{trans}\text{-}H + V{=}O\\
&\quad \rightarrow N_2(g) + H_2O(g) + VOH + V{=}O.
\end{aligned}
$$

4. Discussion

The energies of adsorbed species and transition states involved in the reaction of NO with adsorbed NH_4 species on the V_4-cluster to form N_2 and H_2O are summarized in Table 2 and in Figs. 15a and 15b. The transition state having

Table 2
Energies of intermediate species and transition states with respect to the V_4 cluster and gas-phase NH_3 and NO (TST)

Species	Figure	Energy w.r.t. V_4, NH_3(g), NO(g), kJ/mol
V_4	1a	0
V_4–NH_4	1b	−110
V_4–NH_4–NO TST	5a	+4
V_4–NH_3NHO	5b	−25
V_4–NH_3NHO–V_2	6	−92
V_4–NH_3NHO–Ti_2	7	−58
V_4–NH_3NHO TST	8a	+48
V_4–NH_2NO	8b	−87
V_4 + NH_2NO(g)	–	−42
V_4–NH_2NO	10a	−92
V_4–*trans*-HN=NOH TST	10b	−73
V_4–*trans*-HN=NOH	10c	−82
V_4–*trans*-HN=NOH	11a	−72
V_4–*trans-cis* TST	11b	−50
V_4–*cis*-HN=NOH	11c	−53
V_4–*cis*-HN=NOH TST	12a	−28
V_4–*cis*-HN=NO-*trans*-H	12b	−76
V_4–*cis*-HN=NO-*trans*-H	13a	−61
V_4–N_2–H_2O TST	13b	−57
V_4 + N_2 + H_2O	–	−273

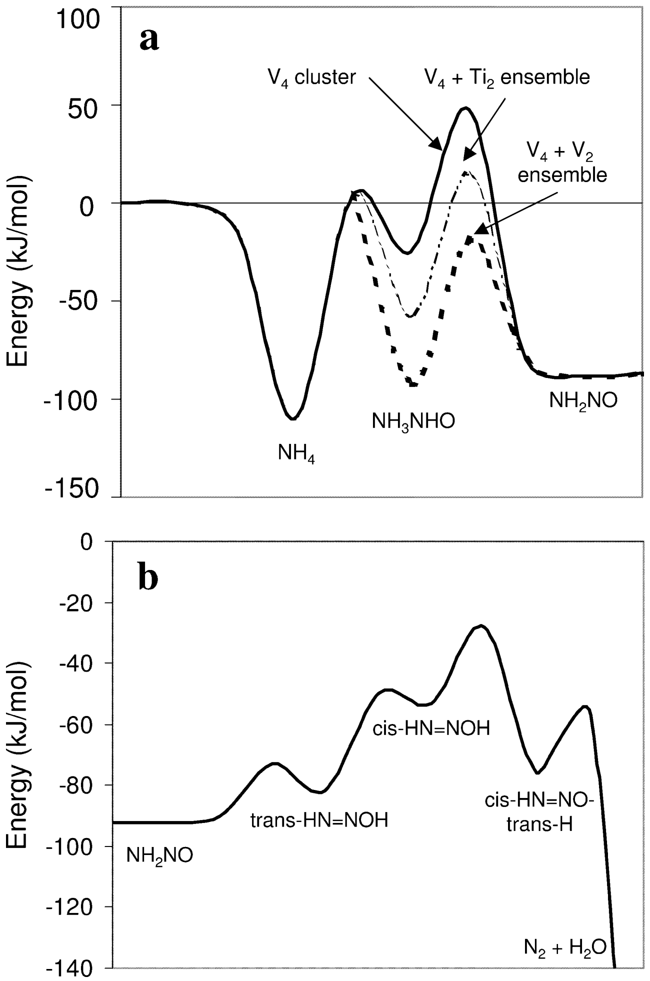

Fig. 15. Potential energy profiles of (a) reaction of NH_3 with NO to form NH_2NO over the V_4 cluster, $V_4 + V_2$ and $V_4 + Ti_2$ ensembles and (b) decomposition of NH_2NO over the V_4 cluster.

the highest energy based on a single vanadia cluster moiety involves the conversion of adsorbed NH_3NHO to form adsorbed NH_2NO, which has an energy of +48 kJ/mol with respect to the V_4 cluster and gas-phase NO and NH_3. The energies of the transition states involved in the subsequent decomposition of adsorbed NH_2NO are much lower in comparison. For example, the transition state having the highest energy for the steps involved in the decomposition of NH_2NO has an energy of −28 kJ/mol with respect to the V_4 cluster and gas-phase NO and NH_3, and this transition state corresponds to the isomerization of *cis*-HN=NOH to *cis*-HN=NO–*trans*-H. Therefore, it appears that the rate of the SCR reaction is controlled by the formation of NH_2NO species rather than by the decomposition of NH_2NO species to form N_2 and H_2O. This conclusion is consistent with the experimental observation that neither NH_2NO nor any other species derived from NH_2NO is observed in significant amounts as a secondary reaction product.

As noted above, the transition state with the highest energy involves the conversion of adsorbed NH_3NHO to give NH_2NO, and this energy is +48 kJ/mol with respect to the V_4-cluster plus gaseous NO and NH_3. We may write the rate of formation of NH_2NO in terms of the following two steps:

$$NH_3 + H^* \leftrightarrow NH_4{}^*, \tag{1}$$

$$NO + NH_4{}^* \rightarrow \text{products}. \tag{2}$$

Step 1 is quasi-equilibrated, with an equilibrium constant $K_{eq,1}$, and the rate constant for step 2 is equal to k_2. The rate of formation of NH_2NO is thus equal to

$$R = k_2 P_{NO} \theta_{NH_4} = K_{eq,1} k_2 P_{NO} P_{NH_3} \theta_*,$$

where θ_{NH_4} is the fractional surface coverage by adsorbed ammonia, and θ_* corresponds to the fraction of the surface that is unoccupied by adsorbed species. If we use a typical value of 10^{-6} atm^{-1} for the preexponential factor of $K_{eq,1}$, and if we use a preexponential factor of 10^8 atm^{-1} s^{-1} for k_2 (as given by collision theory), then the following expression is given for the rate of reaction for concentrations of NO and NH_3 equal to 500 ppm:

$$R = 2.5 \times 10^{-5} \exp(-E_{act}/RT)\theta_* \text{ s}^{-1},$$

where E_{act} is the energy of the transition state with respect to the V_4-cluster and gaseous NO and NH_3. For a value of E_{act} equal to 48 kJ/mol, the rate is equal to about 10^{-9} s^{-1} at 573 K (for a value of θ_* equal to 1). This predicted rate is clearly too low, since a typical turnover frequency [14] for the SCR reaction is of the order of 10^{-3} s^{-1}. Accordingly, the energy of the transition state must be significantly lower than the value of +48 kJ/mol predicted by the DFT calculations on V_4-clusters.

One possible origin for increased stability of the transition state involved in the conversion of adsorbed NH_3NHO to NH_2NO is increased hydrogen bonding of the transition state with V=O and V–OH groups on the catalyst surface. Only hydrogen bonding between vanadia and one side of the NH_3NHO adduct has been considered in the calculation involving a single vanadia cluster. However, hydrogen bonds may be formed between the catalyst and the oxygen atom belonging to the –NHO group or the H atom of the –NH_3 group oriented away from the V_4-cluster. For example, it is known in zeolites [35–38] that stabilization of adsorbate species may take place through extensive hydrogen bonding and/or van der Waals interactions between the transition state and the walls of the zeolite microporous environment. Accordingly, we have examined the possibility that the NH_3NHO adduct (and therefore the transition state for conversion of NH_3NHO to NH_2NO) may be stabilized through hydrogen bonding with a second vanadia moiety oriented on the opposite side of the adduct species, in a geometry that might occur in a catalyst pore. The DFT results show that the additional hydrogen bonding apparently leads to a significant stabilization of the NH_3NHO intermediate. If the same extent of stabilization through hydrogen bonding is assumed for the transition state involved in the conversion of NH_3NHO to NH_2NO, then the energy of the transition state decreases to -19 kJ/mol with respect to gas-phase NH_3 and NO. This energy change gives a rate of formation of NH_2NO species equal to 10^{-3} s^{-1} at 573 K for concentrations of NO and NH_3 equal to 500 ppm, which is consistent with the measured rate of the SCR reaction at these conditions. The calculations show that hydrogen bonding with Ti–OH groups can also lead to some stabilization of the NH_3NHO intermediate, thereby enhancing the rate of the SCR reaction. In addition, we have previously [30] addressed the nature of Brønsted acid sites on vanadia/titania catalyst and found that the adsorption of ammonia to form NH_4 species was facilitated on oligomeric clusters of vanadium oxide containing pentacoordinated vanadium cations. Moreover, the formation of these Brønsted acid sites was shown to be promoted by interaction of vanadium oxide with the titanium oxide support.

We have presently found that the formation of NH_2NO species involves the participation of V=O and V–OH groups, and this process is facilitated by hydrogen-transfer reactions and hydrogen-bonding interactions with vanadium oxide as well as with titanium oxide. Furthermore, the formation of NH_2NO species is facilitated on a material such as vanadium oxide that can accept a hydrogen atom. Thus, the present findings have shown that the formation of NH_2NO species involves the acidic properties (e.g., the formation of NH_4 species from ammonia) and the redox properties (e.g., transfer of a hydrogen atom to the catalyst upon reaction of NO and NH_3 to form NH_2NO) of the catalyst.

The decomposition of NH_2NO species to N_2 and H_2O takes place through a series of hydrogen-transfer reactions with vanadium oxide that can be described as “push–pull” processes in which a hydrogen atom is transferred from vanadium oxide to the adsorbed species while another hydrogen atoms is simultaneously transferred from the adsorbed species to the vanadium oxide. These “push–pull” processes involving reaction with vanadium oxide lead to lower activation energy barriers for isomerization and subsequent decomposition of NH_2NO species to N_2 and H_2O, compared to the gas phase decomposition of NH_2NO, since intramolecular isomerization and decomposition reactions of gaseous NH_2NO involve significant amounts of strain energy in the activated complexes. Thus, the decomposition of NH_2NO species to form N_2 and H_2O must involve a catalyst that can participate in hydrogen-transfer reactions.

The final regeneration of the catalyst after reaction of NH_3 and NO to give N_2, H_2O, and an H-atom on the catalyst involves the formation of H_2O and reoxidation of the catalyst by O_2. For example, formation of H_2O may take place by the reaction of two hydroxyl groups, leading to formation of an oxygen vacancy; and, this oxygen vacancy may be filled by reaction with O_2. The rate of catalyst oxidation by O_2 is however not kinetically significant, since the rate of the SCR does not depend on the O_2 pressure at typical SCR reaction conditions.

5. Conclusions

The present density functional theory calculations using a $V_4O_{16}H_{12}$ cluster have provided insight into the reaction of NO with adsorbed NH_4 species to form N_2, H_2O, and a reduced vanadium oxide cluster ($V_4O_{16}H_{12}$–H) which can then be reoxidized as observed in previous studies. In accordance with earlier experimental observations, ammonia is found to adsorb on the vanadia surface as NH_4 species stabilized between two V=O groups. Nitric oxide is seen to react with the adsorbed NH_4 species to give an NH_3NHO species, which reacts further to give an NH_2NO species. The formation of NH_2NO species by reaction of ammonia and nitric oxide is facilitated by hydrogen bonding of adsorbed species with surrounding vanadia moieties. The NH_2NO species then isomerizes and decomposes to form N_2 and H_2O and a reduced vanadium oxide cluster via a series of steps in which hydrogen atoms are transferred back and forth in a “push–pull” manner from the catalyst surface involving the V=O and V–OH groups to the adsorbed NH_2NO species. The transition state with the highest energy for the reaction of NH_4 species with NO occurs during the formation of the NH_2NO species from NH_3NHO species, which is consistent with the observation that NH_2NO species are not observed on the catalyst surface under reaction conditions. This transition state may be stabilized by extensive hydrogen bonding between the NH_3NHO adduct and surrounding V=O and VOH groups of different vanadia cluster moieties, as well as with TiOH groups of the titania support.

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