

# Cluster molecular modeling of strong interaction for VO<sub>x</sub>/TiO<sub>2</sub> supported catalyst

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Received 11 October 2000; accepted 25 June 2001

## Abstract

Cluster molecular models of VO<sub>x</sub>/TiO<sub>2</sub> catalytic system based on embedding process of V-ion in the anatase support were considered. Cluster structures of (001) anatase surface, containing one- and two-layer were constructed and isomorphous substitution of two Ti-ions on two V-ions were calculated. Comparison of the Brønsted acidic properties of V–OH group on the surface of V<sub>2</sub>O<sub>5</sub> and supported VO<sub>x</sub>/TiO<sub>2</sub> species showed that embedding procedure increases their acidic power and the influence of the second layer of the support is essentially important. Formation of ammonium ion under the adsorption of NH<sub>3</sub> on supported and unsupported vanadium oxide catalyst was considered and discussed. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* VO<sub>x</sub>/TiO<sub>2</sub> supported catalyst; Embedding model; DFT calculations

## 1. Introduction

Vanadia supported catalysts are widely used in industry for the production of sulphuric acid, the selective oxidation of hydrocarbons, the reduction of nitrogen oxides with ammonia and for the production of a number of industrially important bulk and fine chemicals. These catalysts show catalytic properties, which cannot be attributed, either to pure V<sub>2</sub>O<sub>5</sub> or to pure oxide substrate (in our case TiO<sub>2</sub>-anatase). At the same time the influence of the oxide support still remains unanswered in many aspects. Considerable efforts have been devoted to understanding of the structure of the supported catalysts [1]. Amorphous surface layer of a thickness of one to two atomic layers was identified by HRTEM analysis. This amorphous

surface is composed of V-ions embedded in TiO<sub>2</sub> matrix [1]. The support can affect both structural parameters of supported vanadia (epitaxial effects) and electronic structure. The last effect will be mostly pronounced when active component is directly incorporated into the lattice of the support by embedding V-ions in TiO<sub>2</sub>, for example, by the isomorphous substitution of Ti-ions. Namely, such structural model results from the study of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> interface by high-resolution electron microscopy [2].

Epitaxial interaction was considered in the theoretical treatment of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> interface [3]. In [4] a cluster approach (V<sub>2</sub>O<sub>9</sub>H<sub>7</sub> cluster) was used for the investigation of reaction mechanism of the selective catalytic reduction (SCR) of NO by NH<sub>3</sub>. A periodic density functional study of the NH<sub>3</sub> adsorption on the Brønsted and Lewis acid sites of V<sub>2</sub>O<sub>5</sub> was performed in [5]. However, the influence of the support on V<sub>2</sub>O<sub>5</sub> activity was not discussed. In this work we propose cluster molecular models of the VO<sub>x</sub>/TiO<sub>2</sub> catalyst

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based on isomorphous substitution of some surface Ti-ions by V-ions.

## 2. Calculation details

The (001) anatase surface was chosen to model the support. This surface  $\text{TiO}_2$  is thermodynamically stable and appears to be on powder particles. Early papers suggested the good crystallographic fit between (001) $\text{V}_2\text{O}_5$  and (001) $\text{TiO}_2$  anatase enables good “spreading” and coherence of the  $\text{V}_2\text{O}_5$  on the surface of the  $\text{TiO}_2$  [6,7].

Two models of isomorphous substitution of  $\text{Ti}^{4+}$ -ions by  $\text{V}^{4+}$ - and  $\text{V}^{5+}$ -ions were considered. At

first, cluster models of the anatase surface were built. One model is a layer cluster  $[\text{Ti}_6\text{O}_{19}\text{H}_{12}]^{2-}$  (**I**) that included two five-coordinated  $\text{Ti}^{4+}$ -ions (Fig. 1a). Namely, these ions were isomorphically substituted by  $\text{V}^{4+}$ -ions (**II**, Fig. 1b). We took the model with two neighbouring substituted V-ions taking into account that binuclear or polynuclear vanadium oxide structures have been supposed to be more active in the SCR of NO with  $\text{NH}_3$  than isolated  $\text{VO}_x$  species on  $\text{TiO}_2$  support [8,9]. Further oxidation of  $\text{V}^{4+}$ -ions by the water and  $\text{O}_2$  could give rise to structures with two hydroxyl groups on the V-ions or with an OH and a vanadyl groups that were modeled by the clusters  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{12}(\text{OH})_2]^{2-}$  (**III**, Fig. 2a) and  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{13}(\text{OH})\text{O}]^{2-}$  (**IV**, Fig. 2b), respectively.

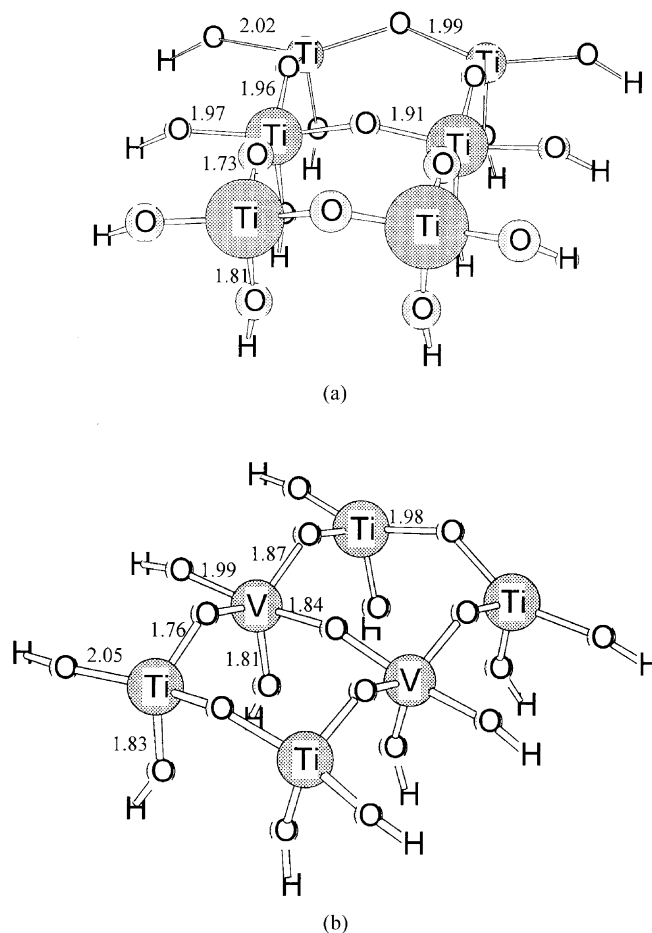


Fig. 1. (a) Cluster model of (001) anatase surface,  $[\text{Ti}_6\text{O}_{19}\text{H}_{12}]^{2-}$  cluster (**I**); (b) cluster model of (001) anatase surface with two V atoms at the lattice positions,  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{12}]^{2-}$  cluster (**II**).

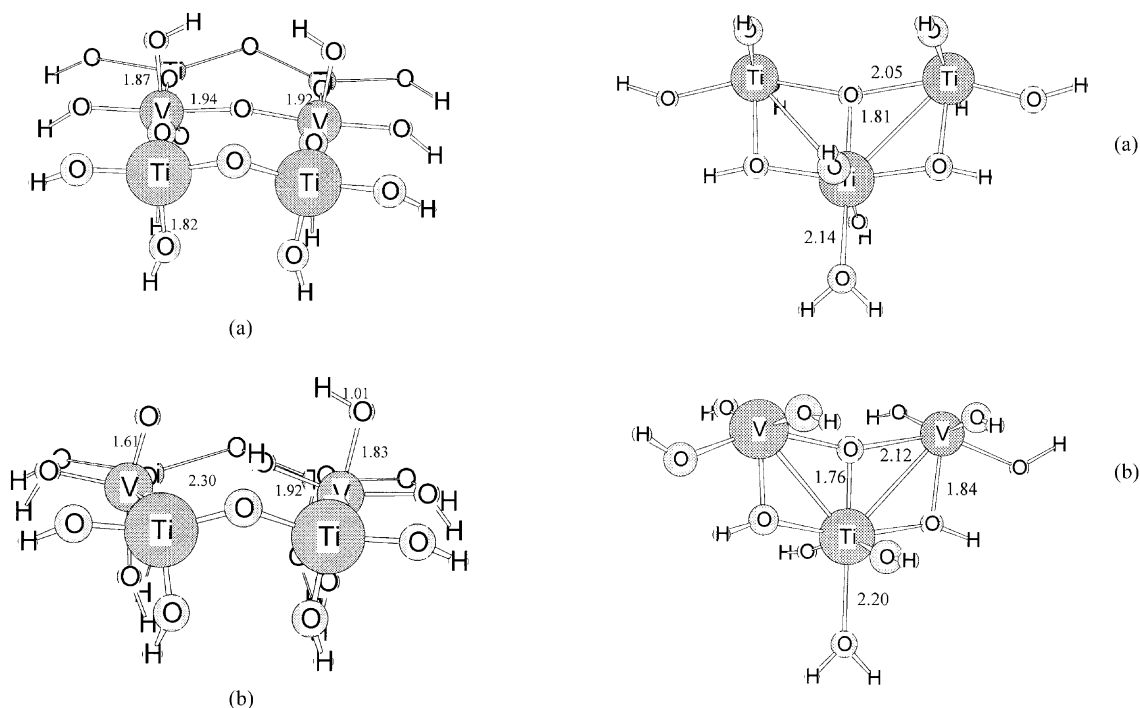


Fig. 2. Cluster models of the active sites of V/TiO<sub>2</sub> surface: (a) [Ti<sub>4</sub>V<sub>2</sub>O<sub>19</sub>H<sub>12</sub>(OH)<sub>2</sub>]<sup>2-</sup> cluster (**III**); (b) [Ti<sub>4</sub>V<sub>2</sub>O<sub>19</sub>H<sub>13</sub>(OH)O]<sup>2-</sup> cluster (**IV**).

Another model represents the part of anatase lattice that contains a Ti<sup>4+</sup>-ion in the bulk coordination and two surface five-coordinated Ti<sup>4+</sup>-ions; this is the two-layer cluster Ti<sub>3</sub>O<sub>12</sub>H<sub>12</sub> (**V**, Fig. 3a). The cluster model of the supported catalyst TiV<sub>2</sub>O<sub>12</sub>H<sub>12</sub> (**VI**, Fig. 3b) was generated from (**V**) cluster by substitution of Ti<sup>4+</sup> surface ions by V<sup>4+</sup>-ions. In the cluster TiV<sub>2</sub>O<sub>14</sub>H<sub>14</sub> (**VII**, Fig. 3c) a hydroxyl group and a vanadyl group are presented on the surface cluster with the two V<sup>5+</sup>-ions.

To compare the properties of the supported catalyst V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and pure V<sub>2</sub>O<sub>5</sub>, the calculations of [V<sub>2</sub>O<sub>9</sub>H<sub>7</sub>]<sup>1-</sup> cluster (**VIII**) were carried out. In this cluster one V<sup>5+</sup>-ion possesses OH and vanadyl groups are connected to another V center.

At the beginning, clusters (**I**) and (**V**) were constructed with experimental values of bond lengths  $R(\text{Ti}-\text{O}_1) = 1.979$  and  $R(\text{Ti}-\text{O}_2) = 1.932$  Å. The broken bonds at the clusters boundaries were saturated with hydrogen atoms. Experimental geometries of

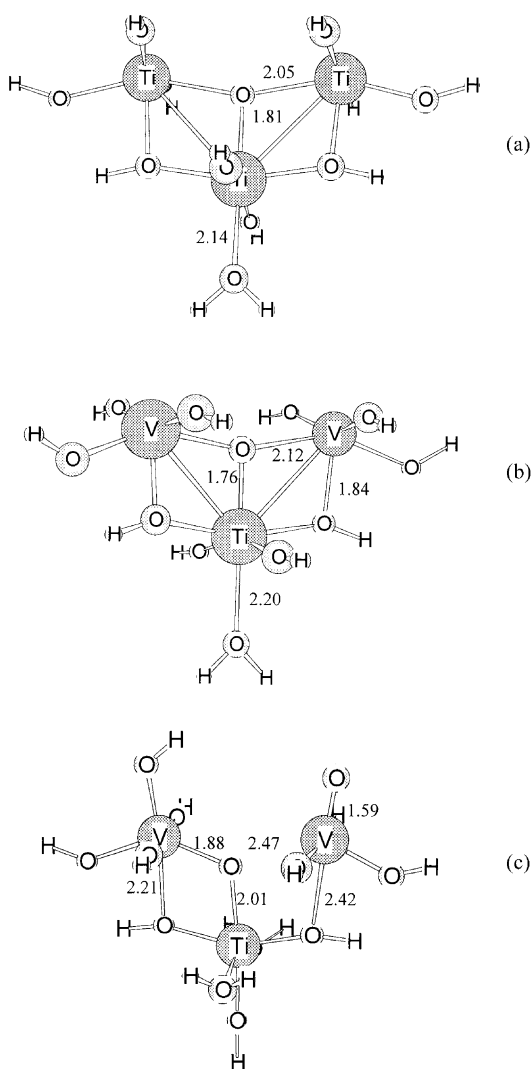


Fig. 3. Models of the two layers clusters: (a) Ti<sub>3</sub>O<sub>12</sub>H<sub>12</sub> two layers cluster (**V**); (b) TiV<sub>2</sub>O<sub>12</sub>H<sub>12</sub> cluster model of the supported catalyst (**VI**); (c) TiV<sub>2</sub>O<sub>14</sub>H<sub>14</sub> cluster with a hydroxyl and vanadyl groups on the surface (**VII**).

the clusters were chosen and the boundary H\* atoms were placed in the direction of the neighbouring Ti atoms of anatase lattice on the distances equal to 1 Å. Then, positions of the boundary H\* atoms were fixed and the cores of the clusters were optimized. All the other clusters generated by isomorphous substitution Ti<sup>4+</sup>-ions by V<sup>4+</sup> and V<sup>5+</sup> were optimized in Cartesian coordinates with frozen positions of boundary

H\* atoms. In order to check the influence of the rigidity of the lattice on the results some calculations were also performed with frozen positions of OH boundary groups in the framework of above-described approach.

Through the whole paper we have discussed only thermodynamic aspects of structural variations of the system under question. According to this approach of the paper we also did not consider the reaction path of ammonium ion formation, but only the comparative stability of one for different structures of the catalyst.

The density functional (DFT) calculations were performed using the ADF program [10–12]. Geometry optimization was carried out with the Vosko–Wilk–Nusair (VWN) local-type functional [13], the energies of structures and energy of water adsorption were computed using the Becke–Perdew (BP86) non-local type functional [14,15]. The geometry optimization of ammonium ion formation was performed on the BP86 level of theory. Molecular orbitals were expanded into a set of Slater-type exponential basis functions centered on the atoms. Single-zeta basis set without polarization functions corresponding to I-type of basis set in ADF program was used for H\* atoms. For the calculations of the NH<sub>4</sub><sup>+</sup>-ion formation, the IV-type basis set for H atoms of ammonia and interacting V–OH groups were used. In this type of basis set a polarization function is added for H. The II-type basis set was used for V and Ti atoms. It corresponds to double-zeta basis sets without polarization functions and a triple-zeta set for 3-D shells of the first row of the transition metals. Double-zeta basis sets extended with a polarization function (III-type of basis set) were used for O and N atoms. Since calculated systems have large sizes we froze the inner-core orbitals of the atoms except for hydrogen, i.e. 1S was frozen for oxygen and nitrogen and 1S2S2P for vanadium and titanium. Fitness of chosen basis set was tested on small [(HO)VO(OH\*)<sub>2</sub>] cluster structure and NH<sub>3</sub> molecular.

Calculations have been performed with using of non-relativistic approach. To eliminate convergence problems in some cases, we allowed partial occupancies for highest orbitals using smear values 0.01 hartree. Final solutions were verified on the absence of partial occupations of MO.

### 3. Results and discussion

Cluster models of the (001) anatase surface and their isomorphically V-substituted structures are shown in Figs. 1 and 3. The geometrical structure of the one-layered cluster (**I**) is presented in Fig. 1a. Relaxation of anatase surface (001) was revealed at optimization of the clusters geometry; namely, surface Ti-ions are shifted into the crystal depth relative to surface O-ions. The distance between Ti atoms and located below oxygen atoms is decreased to 1.785 Å for internal Ti-ions in the cluster and 1.81 Å for boundary ones (see Fig. 1a). This agrees with experimental data on the relaxed surface structure [16]. So, calculated relaxation of the atoms on the anatase surface is about 10%, that is close to experimental one.

To test the chemisorption properties of the cluster (**I**) we calculated the energy of H<sub>2</sub>O molecule bonding with anatase surface. Adsorbed complex is shown in Fig. 4. The adsorption energy ( $E_{\text{ads}}$ ) has been calculated according to the expression

$$E_{\text{ads}} = E_{(\text{adsorbate}/\text{substrate})} - (E_{\text{adsorbate}} + E_{\text{substrate}})$$

where  $E_{(\text{adsorbate}/\text{substrate})}$ ,  $E_{\text{adsorbate}}$ , and  $E_{\text{substrate}}$  are the total energies of the adsorbate/substrate system, isolated adsorbate, and substrate, respectively. A negative  $E_{\text{ads}}$  value corresponds to a stable adsorbate/substrate system. The energy of molecular

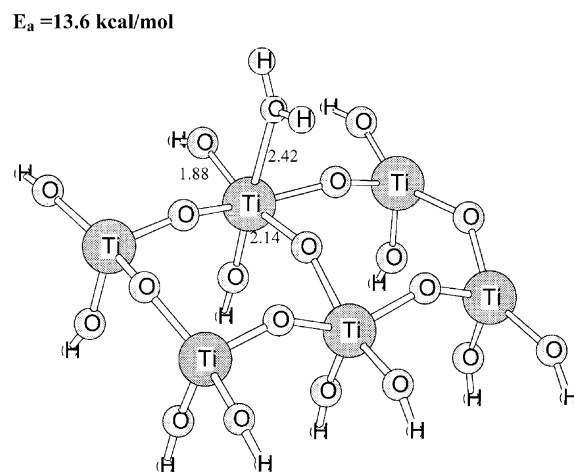


Fig. 4. H<sub>2</sub>O molecular adsorption on [Ti<sub>6</sub>O<sub>19</sub>H<sub>12</sub>]<sup>2-</sup> cluster.

adsorption of H<sub>2</sub>O was found 13.6 kcal/mol, what is in good agreement with experimental estimates at 12–18 kcal/mol [17].

Further, we considered the cluster models of the active center of VO<sub>x</sub>/TiO<sub>2</sub> catalyst according to proposed above hypothesis on their formation. The optimized structure of the cluster containing in the surface layer 2 isomorphous substituted V<sup>4+</sup>-ions in the positions of Ti<sup>4+</sup>-ions is shown in Fig. 1b. As it was found, changes of structural parameters of the surface at isomorphous substitution are not substantial (Fig. 1a and b). All bond distances are changed in the interval from –0.02 to +0.09 Å with isomorphous substitution of Ti<sup>4+</sup> atoms by V<sup>4+</sup>. Distance between two Ti atoms in initial cluster does not decrease significantly by isomorphous substitution on V atoms; that changes from 3.74 to 3.63 Å. This confirms the supposition on the possible incorporation of V-ions into the lattice positions of Ti-ions of the anatase surface. This presumably arises from very closely similar cation radii of 0.58 Å for V<sup>4+</sup> and 0.61 Å for Ti<sup>4+</sup>. Cation radii of V<sup>5+</sup> and Ti<sup>4+</sup> are also close. That of V<sup>5+</sup> equals to 0.54 Å [18].

To elucidate a stability of such structures and a possibility of their transformations into other active structures, we studied cluster (III) with neighbouring hydroxyl groups on each V atoms. The optimized structure is shown on Fig. 2a. Distance between two V<sup>5+</sup>-ions equals 3.86 Å that is larger by the value 0.12 Å compared to Ti...Ti distance in the initial cluster. The largest variation in the geometry equals to 0.13 Å. Bond length R(V–OH) (where the boundary H atom models lower layer) increases to 1.92 Å compared to 1.79 Å in cluster (I). There are no essential changes in the other geometric parameters on the isomorphous substitution Ti<sup>4+</sup> atoms by V<sup>5+</sup>–OH groups.

To obtain more detailed mechanistic insight, Topsøe et al. [19] employed in situ FTIR and on-line mass spectrometry to study the surface species and the gaseous reaction products when pre-adsorbed ammonia on vanadia/titania catalysts was exposed to either NO + O<sub>2</sub>, NO, or O<sub>2</sub> under temperature-programmed reaction condition. It was found that Lewis and Brønsted acid sites are presented on the surfaces of these catalysts, with the Brønsted acid sites being associated with V<sup>5+</sup>–OH species. The new hydroxyl band

around 3600–3700 cm<sup>–1</sup> was observed by Topsøe et al. [19,20] and Adams et al. [21], through the SCR reaction pathway. It was assigned as a hydroxyl on a reduced vanadium center, V<sup>4+</sup>–OH. The number of mechanistic schemes of the SCR of NO by NH<sub>3</sub> has been proposed in the literature [19,20]. In some cases, the catalytic activity, as it was found, to be related to the ammonia adsorbed on the Brønsted acid sites associated with V<sup>5+</sup>–OH sites [19–24]. V<sup>5+</sup>=O groups are also involved in the reaction, and specifically in the activation of adsorbed ammonia. The cluster, which could describe such active site, is shown on the Fig. 2b, one was formed from the structure (III) by transfer of H atom of one of OH groups to the bridged Ti–O–Ti, Ti–O–V or V–O–V oxygen. This resulted in the formation of the structure with neighbouring V=O and OH groups. Such transfer of H atom is exothermic process. For the case of H atom transfer to V–O–V bridged oxygen the gain of energy is –40.5 kcal/mol for the calculations with frozen positions of boundary H\* atoms and –20.9 kcal/mol for the one with frozen positions of boundary OH groups. The final distances between V atoms increased to 4.7 and 4.2 Å, respectively.

Formation of the active site containing two neighboring V=O groups could be suggested as transitions of both H atoms of V–OH groups of the structure (III) to bridged oxygens. Another way of the formation of such type of the site ([Ti<sub>4</sub>V<sub>2</sub>O<sub>18</sub>H<sub>12</sub>O<sub>2</sub>]<sup>2–</sup> cluster) is the H<sub>2</sub>O molecule desorption from (III) resulting in the appearance of the structure with V=O oxygen on every V atom and oxygen vacancy between them. This process is energetically favored, ΔE = –31.6 and –4.3 kcal/mol for two above-mentioned choices of boundary conditions, respectively, with the resulting distance between V atoms of 5.04 and of 4.36 Å.

As in the previous case of monolayer cluster (I), the change of optimized geometry of two-layer cluster (V) due to isomorphous substitution of two Ti<sup>4+</sup> by V<sup>4+</sup> was rather small (Fig. 2b, VI). The bond lengths R(Ti–O) and R(V–O) differ by 0.07 Å for the bridge oxygen, on 0.04 Å for the boundary oxygen and 0.04–0.06 Å for the bulk O. The structure was changing; when (V) centers were in the +5 oxidation state in (VII) model (see Fig. 3c). The bond length between vanadium atom and bulk oxygen increased to 2.4 Å.

The calculated bond length of the vanadyl group is 1.6 Å.

It is suggested that a key step in the SCR reaction is the activation of the  $\text{NH}_3$  adsorbed. There is debate over the nature of the activated form of adsorbed  $\text{NH}_3$ . The question as to whether the adsorbed  $\text{NH}_3$ , which is active for the reduction of  $\text{NO}$ , is adsorbed on the surface as dissociate or molecular adsorbed  $\text{NH}_3$ , or as an  $\text{NH}_4^+$ -ion, has not been fully verified experimentally. Many groups report that the SCR reaction requires ammonia adsorbed on Brönsted acid sites as an ammonium ion [19–24]. Moreover, ammonia adsorption on the oxide catalysts is the test on the detection of Brönsted acid sites. The ammonia adsorption was calculated for isomorphous substituted monolayer cluster  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{13}(\text{OH})\text{O}]^{2-}$ , two-layer cluster  $\text{TiV}_2\text{O}_{14}\text{H}_{14}$  and  $[\text{V}_2\text{O}_9\text{H}_7]^-$  cluster modeling pure  $\text{V}_2\text{O}_5$ . Results of these calculations are shown in Fig. 5 and in Table 1. According to calculations, the formation energy of  $\text{NH}_4^+$ -ion is larger for  $\text{TiV}_2\text{O}_{14}\text{H}_{14}$  cluster ( $\Delta E = -9.9$  kcal/mol) compared to  $\Delta E = -7.2$  kcal/mol for  $[\text{V}_2\text{O}_9\text{H}_7]^-$ . This agrees well with  $\text{NH}_3$  desorption enthalpies derived from temperature-programmed desorption measurements (18–26 [25] and 22–28 kcal/mol [26]) carried out for vanadia- and titania-supported vanadia. Charge of  $(\text{NH}_4)^{x+}$ -ion is larger for the supported catalyst. The formation energy of  $\text{NH}_4^+$ -ion for monolayer cluster  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{13}(\text{OH})\text{O}]^{2-}$  equals  $\Delta E = +0.5$  kcal/mol. Thus, the quantum-chemical calculations of  $\text{NH}_3$  adsorption on pure  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts confirm the presence of Brönsted acid sites on these catalysts and the rise of acidity of the supported catalyst compared to pure  $\text{V}_2\text{O}_5$ . It is necessary to mention that the adsorption complexes were calculated in the framework of  $C_{2v}$  and  $C_s$  symmetries. In both cases  $\text{NH}_4^+$ -ions were formed and energies of their formation were close. Comparison of the  $\text{NH}_3$  adsorption energies on monolayer and two-layer clusters points to an importance of lower layer. The influence of neighboring Ti atoms in the layer on the adsorption energy is not so considerable.

Calculations of the dissociate ammonia adsorption on  $[\text{Ti}_4\text{V}_2\text{O}_{18}\text{H}_{12}\text{O}_2]^{2-}$  cluster were carried out as well. Fig. 6 shows optimized geometry of the adsorption complex obtained with fixed  $\text{H}^*$  and O atoms in initial cluster. As a result this reac-

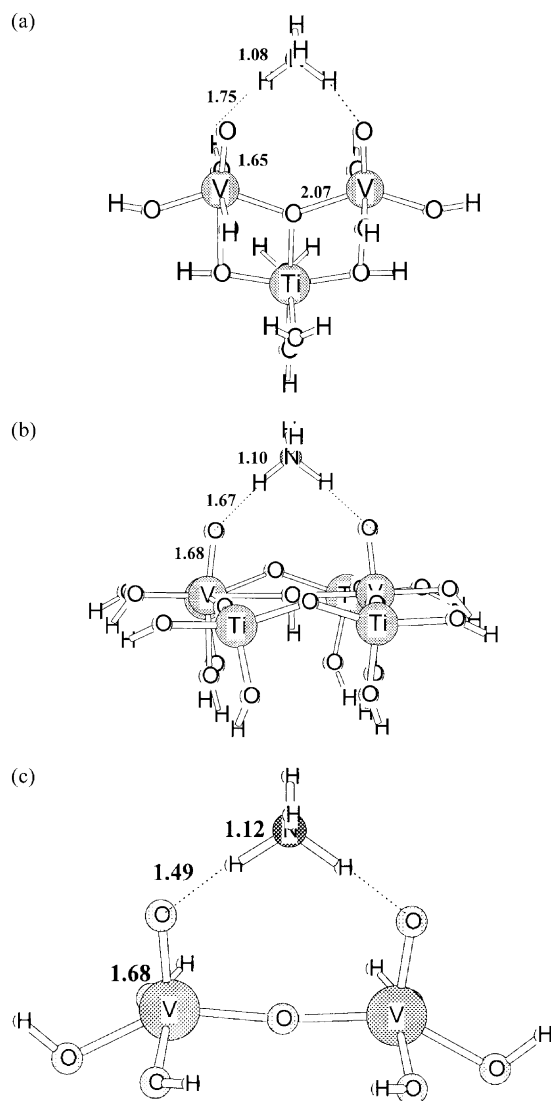


Fig. 5.  $\text{NH}_3$  adsorption on (a) two layers cluster  $\text{TiV}_2\text{O}_{14}\text{H}_{14}$ ; (b) isomorphous substituted monolayer cluster  $[\text{Ti}_4\text{V}_2\text{O}_{19}\text{H}_{13}(\text{OH})\text{O}]^{2-}$ ; (c)  $[\text{V}_2\text{O}_9\text{H}_7]^{1-}$  cluster (VIII) modeling pure  $\text{V}_2\text{O}_5$ .

tion is endothermic ( $\Delta E = +81.9$  kcal/mol) for fixed  $\text{H}^*$  atoms. When positions of  $\text{H}^*$  and O atoms are fixed this reaction is endothermic also ( $\Delta E = +39.6$  kcal/mol). These estimations are in agreement with the experimental data that the band corresponding to the amide species  $\text{NH}_2$  has not been detected [27].

Table 1  
Charges and bond lengths for the adsorption complexes with NH<sub>3</sub><sup>a</sup>

Charges and distances (Å)	[V <sub>2</sub> O <sub>9</sub> H <sub>7</sub> ] <sup>-</sup> + NH <sub>3</sub>	TiV <sub>2</sub> O <sub>14</sub> H <sub>14</sub> + NH <sub>3</sub>	[Ti <sub>4</sub> V <sub>2</sub> O <sub>21</sub> H <sub>14</sub> ] <sup>2-</sup> + NH <sub>3</sub>
<i>q<sub>v</sub></i>	2.0906	2.0561	2.0279
<i>q<sub>o</sub></i>	-0.8454	-0.7988	-0.7837
<i>q<sub>H...O</sub></i>	0.3180	0.3237	0.3273
<i>q<sub>H(N)</sub></i>	0.2482	0.2834	0.2581
<i>q<sub>N</sub></i>	-0.4776	-0.4356	-0.4516
<i>q<sub>(NH<sub>4</sub>)<sup>+</sup></sub></i>	0.6548	0.7786	0.7192
<i>d<sub>N-H(N)</sub></i>	1.02	1.03	1.03
<i>d<sub>N-H(O)</sub></i>	1.12	1.08	1.10
<i>d<sub>O-H</sub></i>	1.49	1.75	1.67
<i>E<sub>ads</sub></i> (kcal/mol)	-7.2	-9.9	+0.5

<sup>a</sup> DFT calculations were performed on the BP86 level.

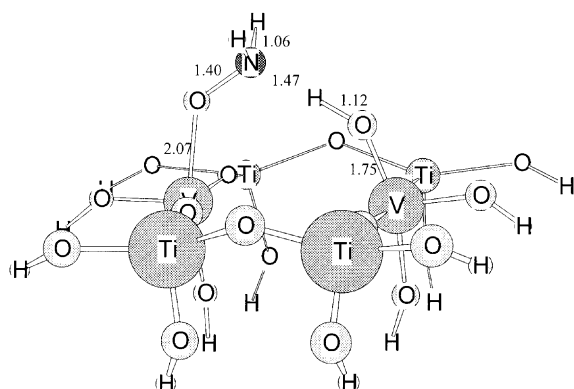


Fig. 6. Dissociative ammonia adsorption on [Ti<sub>4</sub>V<sub>2</sub>O<sub>18</sub>H<sub>12</sub>O<sub>2</sub>]<sup>2-</sup> cluster. Optimized geometry of the adsorption complexes.

#### 4. Conclusions

In this work we considered cluster molecular models of the VO<sub>x</sub>/TiO<sub>2</sub> catalyst based on the embedding process of V-ions in the anatase support. One- and two-layer cluster structures of (001) anatase surface were constructed. The cluster models of the supported catalyst were generated by isomorphous substitution of two Ti-ions by two V-ions. In order to check the influence of the rigidity of the lattice on the results some geometries of these clusters were optimized with the frozen positions of the boundary OH groups and the frozen positions of the boundary hydrogen atoms. It was found that two approaches in the optimization of the clusters give qualitatively the same results.

We have shown also that supported VO<sub>x</sub>/TiO<sub>2</sub> catalyst system exhibits increased acidic power compared to the pure V<sub>2</sub>O<sub>5</sub>. The changes in the acidic power of the supported VO<sub>x</sub>/TiO<sub>2</sub> system were illustrated by the NH<sub>3</sub> adsorption with the formation of an ammonium ion. Comparison of the NH<sub>3</sub> adsorption energies on monolayer and two-layers clusters points out the large importance of the lower layer compared to the extension of the cluster size in the same layer.

#### Acknowledgements

This work was done under support of the INTAS (Grant IR-97-0059) “theoretical and experimental investigation of a catalytic activity of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> system” and RFBR 00-15-97441.

#### References

- [1] J.C. Vadrine, Catal. Today 56 (2000) 455.
- [2] G.N. Kryukova, D.O. Klenov, G.A. Zenkovets, React. Kinet. Catal. Lett. 60 (1997) 179.
- [3] D.C. Sayle, C.R.A. Catlow, M.-A. Perrin, P. Nortier, J. Phys. Chem. 100 (1996) 8940.
- [4] F. Gilardoni, J. Weber, A. Baiker, J. Phys. Chem. A 101 (1997) 6069.
- [5] X. Yin, H. Han, I. Gunji, A. Endou, S.S.C. Ammal, M. Kubo, A. Miyamoto, J. Phys. Chem. B 103 (1999) 4701.
- [6] A. Vejux, P. Courtine, J. Solid State Chem. 63 (1986) 179.
- [7] Z.X. Liu, Z.D. Lin, H.J. Fan, F.H. Li, Q. Bao, S. Zhang, Appl. Phys. A 45 (1988) 159.
- [8] F. Janssen, F. Van den Kerkhof, H. Bosch, J.J. Ross, Phys. Chem. 91 (1987) 6633.

- [9] U.S. Ozkan, Y. Cai, M.W. Kumthekar, L. Zhang, *J. Catal.* 142 (1993) 182.
- [10] ADF 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam, E.J. Baerends et al., *Chem. Phys.* 2 (1973) 41.
- [11] G. te Velde, E.J. Baerends, *J. Comp. Phys.* 99 (1992) 84.
- [12] C. Fonseca Guerra et al., *METECC-95* (1995) 305.
- [13] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [14] A.D. Becker, *Phys. Rev. A* 38 (1988) 3098.
- [15] J.P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B* 33 (12) (1986) 8822.
- [16] G. Charlton, P.B. Howes, C.L. Nicklin, P. Steadman, J.S.G. Taylor, C.A. Muryn, S.P. Harte, J. Mercer, R. McGrath, D. Norman, T.S. Turner, G. Thornton, *Phys. Rev. Lett.* 78 (1997) 495.
- [17] G. Munuera, F. Moreno, F. Gonzalez, Reactivity of solids, in: *Proceedings of the 7th International Symposium Reaction Solids*, Chapman & Hall, London, 1972, p. 681.
- [18] *Handbook of Chemistry and Physics*, 73rd Edition, CRC Press, Boca Raton, 1992–1993.
- [19] N.-Y. Topsøe, H. Topsøe, J. Dumesic, *J. Catal.* 151 (1995) 226.
- [20] N.-Y. Topsøe, H. Topsøe, J. Dumesic, *J. Catal.* 151 (1995) 241.
- [21] R.C. Adams, L. Xu, K. Moller, T. Bein, W.N. Delgass, *Catal. Today* 33 (1997) 263.
- [22] M. Inomata, A. Miyamoto, Y. Murakami, *J. Catal.* 62 (1980) 140.
- [23] A. Miyamoto, K. Kobayashi, M. Inomata, Y. Murakami, *J. Phys. Chem.* 86 (1982) 2945.
- [24] N.Y. Topsøe, *Science* 265 (1994) 1217.
- [25] T.Z. Smak, G.A. Dumesic, B.S. Clausen, E. Tornquist, N.-Y. Topsøe, *J. Catal.* 135 (1991) 246.
- [26] A.M. Efstathion, K. Fliatoura, *Appl. Catal. B* 6 (1995) 35.
- [27] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B: Environ.* 18 (1998) 1.