

Role of electronic structure of vanadium oxide cluster in methanol oxidation

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ABSTRACT To reveal the catalytic activity of neutral vanadium oxide nanoclusters in methanol (CH₃OH) oxidation, quantum chemical simulation of methanol adsorption on V₄O₁₀ cluster and further oxidation to formaldehyde (CH₂O) is performed at DFT PBE level. According to calculation, the cluster has a tetrahedral cage structure with four terminal V=O(t) and six bridging V–O(b)–V fragments. The reaction of methanol and V₄O₁₀ occurs through association and two abstraction stages sequentially. The role of the two oxygens O(t) and O(b) in these processes is shown to be different. Analysis of atomic charges and electron density in V₄O₁₀ allowed to explain the observed patterns and predict the reduction of the activation barrier of rate-determining step of (CH₂O)V₄O₁₀H₂ formation when the V₄O₁₀ has positive charge or titanium is introduced into the cluster's structure.

KEYWORDS transition metal oxide cluster, methanol oxidation, V₂O₅, mechanism, oxygen radical, activation energy, transition state

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1. Introduction

Transition metal oxide nanoclusters are used in various fields of science including catalysis, materials science, and medicine [1–3]. These small clusters contain low-coordinated metal atom, large surface area, oxygen radicals and vacancies which is responsible for their unique properties [4]. They are a common model of active sites in nanostructured catalysts for studying the mechanisms of heterogeneous catalytic reactions [5, 6]. Fundamental information on the mechanism of catalytic reactions and the structure of active sites is necessary for the targeted design of effective catalysts, which is important for the development of technologies that comply with the principles of energy conservation and green chemistry.

Various experimental and theoretical methods are commonly employed to determine the structure of metal oxide clusters. Significant progress in structure clarification was achieved through beam methods and quantum chemical methods. For instance, V_mO_n⁺ ($m = 1 \div 4$, $n = 1 \div 11$) were synthesized [7], the composition and growth dynamics of vanadium oxide clusters were recorded [8]. The structures of V_mO_n and V_mO_n⁺ ($m = 2 \div 4$, $n = 2 \div 10$) were calculated by different quantum-chemical methods including UHF, B3LYP and BP86 [9–12]. The authors considered various isomers including chain, cyclic, and fragments of vanadium oxide crystal lattice, and demonstrated that for V₄O₁₀ the tetrahedral structure with pronounced closed-cage character is the most energetically stable. In addition to V_mO_n structures, the reaction of vanadium oxide clusters with stable molecules (such as CH₄, C₂H₆, CCl₄, C₂H₄) was also studied [13–16]. For instance, it was demonstrated that tetranuclear V₄O₁₀⁺ can activate C–H bond in methane with low activation energy (37 kJ/mol) and catalyzes methane oxidation to CH₃OH [13]. Further oxidation of methanol on vanadium oxide clusters appears promising for further investigation.

Vanadium oxide-based materials catalyze methanol oxidation to produce useful chemical products, such as formaldehyde (CH₂O), dimethoxymethane (CH₂(OCH₃)₂), methyl formate (HCOOCH₃), dimethyl ether (CH₃OCH₃), formic acid (HCOOH) with high selectivity [17, 18]. The reaction, also known as methanol oxidative dehydrogenation, has been studied on vanadium oxide [19–23]. The Mars-van Krevelen redox cycle is accepted as the reaction mechanism, where the rate-determining step is the C–H bond cleavage in the methoxide intermediate leading to the formation of adsorbed CH₂O [20, 21]. This step is determined by many factors including the structure and charge of the V₂O₅ active site. The surface of the catalysts is not uniform. Different forms of vanadium oxide were observed on the support including isolated VO_x samples, polymeric (VO_x)_n species and 3D particles such as clusters or crystallites [22, 23]. The most active catalysts in methanol oxidation were V₂O₅/ZrO₂ and V₂O₅/TiO₂ with monomeric and polymer particles, as opposed to V₂O₅/SiO₂, in which all the vanadium was in the bulk phase. An inverse correlation between catalytic activity and the

content of the bulk phase was observed. It can be assumed that small vanadium oxide clusters, i.e. model V_4O_{10} , will act as an active site and catalyze the oxidation of methanol.

To test this hypothesis, a quantum chemical simulation of methanol oxidation to formaldehyde on model V_4O_{10} was performed at DFT PBE level. To elucidate the catalytic activity of the cluster, structure, energy changes and activation energy at each step of methanol oxidation were calculated including C–H bond cleavage in the methoxide intermediate. Particular attention is paid to the influence of electronic effects on the stability of the formed intermediates and the activation energy.

2. Calculation details

To simulate methanol oxidation on V_4O_{10} , structures of the clusters, CH_3OH , and all intermediates were fully optimized and the energies were calculated using the spin-polarised DFT method with PBE functional [24]. The Dirac–Coulomb–Breit Hamiltonian with separate spin-free and spin-dependent components was applied [25]. The energy-optimized extended Gaussian basis set of triple-polarized quality of the large component, and the corresponding kinetically balanced basis for the small component was used [26]: V [26s23p16d5f/7s6p4d1f], O [10s7p3d/3s2p1d], C [10s7p3d/3s2p1d], and H [6s2p/2s1p].

The reaction pathways were preliminarily analyzed by scanning the potential energy surface along the reaction coordinate. The exact transition state (TS) structure was determined by eigenvector following using the Berny algorithm [27]. To confirm the TS structure, intrinsic reaction coordinate (IRC) calculations [28] were performed by following the single imaginary mode. Atomic charges were calculated using overlap populations analysis (Mulliken scheme, MS) and analysis of atomic partitions of the density (Hirshfeld scheme, HS). All calculations were performed by the Priroda software package [29]. The method was successfully applied in the theoretical study of the structure and simulation of catalytic properties of metal nanoclusters [30–32].

3. Results and discussion

The V_4O_{10} cluster is considered as a model of the active site of a heterogeneous catalyst containing vanadium oxide for methanol oxidation. According to previous calculations [10, 33], it has a tetrahedral cage structure with four terminal $V=O(t)$ and six bridging $V-O(b)-V$ fragments. Molecular geometry calculated by our method is shown in Fig. 1. The structure and interatomic distances agree with both the recent calculation of V_4O_{10} at B3LYP/TZVP level [12] and with previously theoretical study at B3LYP/6-31G* level [11]. The minimum-energy structure has a singlet electronic state and closed electron shells. Atomic charge calculation for V_4O_{10} using both MS and HS approaches reveals that all vanadium atoms have the same positive charge. The O(t) and O(b) differ in charge: all bridging oxygen atoms possess higher negative charge (–0.500 MS and –0.232 HS) than terminal oxygens (–0.288 MS and –0.203 HS). The O(t) and O(b) differ in interatomic V–O distances: V–O distances in terminal fragments are 1.60 Å; calculated V–O distances in bridging fragments are 1.81 Å. Analysis of molecular orbitals of V_4O_{10} demonstrates that the isosurfaces of HOMO are localized on two oxygen atoms. Both oxygen O(t) and O(b) sites are likely to be active in hydrogen binding as a result of oxidative dehydrogenation of methanol.

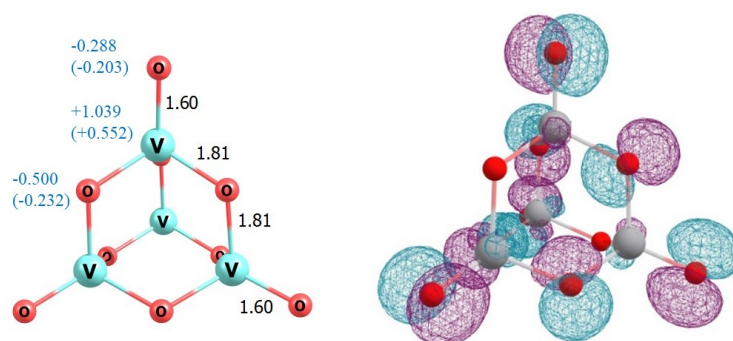


FIG. 1. Left picture: optimized structure with calculated interatomic distances (colored by black), MS and HS atomic charges (colored by blue). Right picture: HOMO of V_4O_{10}

The CH_3OH oxidation to CH_2O on neutral V_4O_{10} cluster is simulated. The process occurs through several steps involving association of methanol with cluster (1), abstraction of the first hydrogen from –O–H group (2) and abstraction of the second hydrogen atom from – CH_3 group (3) to form product CH_2O : $CH_3OH + V_4O_{10} \rightarrow (CH_3OH)V_4O_{10} \rightarrow (CH_3O)V_4O_9OH \rightarrow (CH_2O)V_4O_8(OH)_2$

The structures of the optimized complexes formed in steps 1, 2 and 3, as well as the transition state of step 3 are shown in Fig. 2. The thermodynamic and kinetic parameters of each stage including energy changes and activation energies are

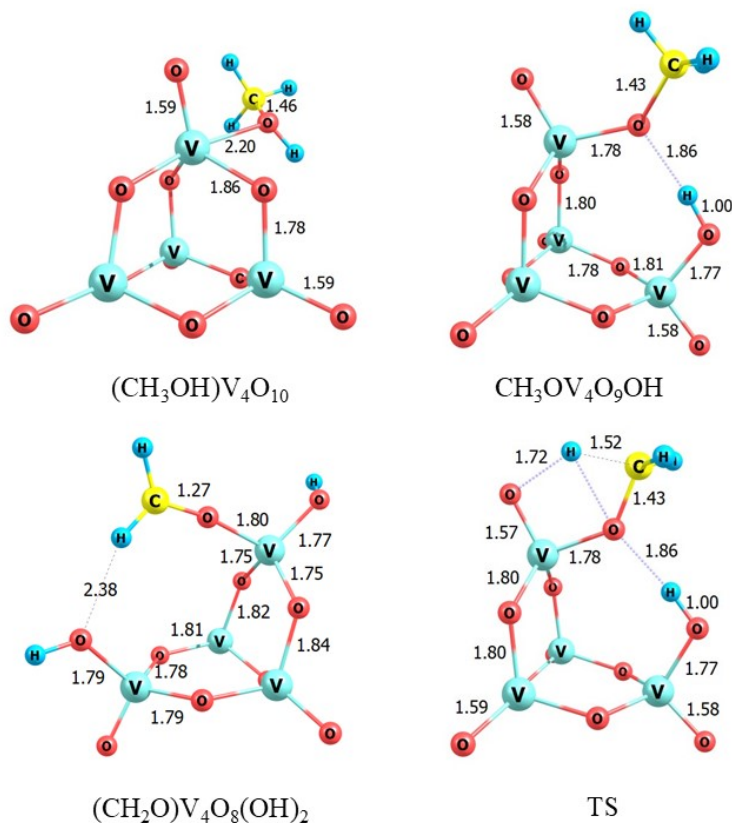


FIG. 2. Optimized structures and calculated interatomic distances in complexes and transition state of the steps 1–3 in CH₃OH oxidation to CH₂O on neutral V₄O₁₀ cluster

considered below. Association product (CH₃OH)V₄O₁₀ is formed spontaneously on V site via –OH coordination with an energy gain of –59.3 kJ/mol.

This coordination of the alcohol molecule is due to a positive charge on the vanadium ion. The second step of methanol oxidation involves the abstraction of the first hydrogen. The dissociative adsorption of CH₃OH on the clusters occurs through O–H bond cleavage in hydroxyl group and breaking the V–O–V fragment. The formation of (CH₃O)V₄O₉OH complex is energetically favorable by 55.4 kJ/mol compared to association product (CH₃OH)V₄O₁₀ and 114.7 kJ/mol compared to an isolated gas-phase cluster and methanol. A proton in (CH₃O)V₄O₉OH is attached to the oxygen, while the methoxy group is coordinated to the vanadium atom. A similar mechanism of the dissociative addition of methanol on vanadium surface with the saving of the valence of the vanadium atom was predicted previously [33]. Further abstraction of the second hydrogen atom from CH₃– group to form product (CH₂O)V₄O₁₀H₂ occurs on terminal O(t) site increasing total energy on 130 kJ/mol in relative to energy of (CH₃O)V₄O₉OH). Calculated activation barrier is high (189 kJ/mol) due to the need to destroy the strong cage structure of the cluster. High activation energy, 147 kJ/mol, of the step CH₃–O– → CH₂–O– + H– was also predicted previously on vanadium oxide monolayer [33].

It seems interesting to analyze the atomic charges on the key atoms V(1), O_b(2), O_t(3), O(4) and C(5) in the complexes involved in the stages 1–3 (Fig. 3). Compared to the original V₄O₁₀ cluster, vanadium in the complexes is in a reduced state throughout the oxidation process. This is consistent with experimental studies of the methanol oxidation mechanism [22], according to which vanadium is reduced from V⁺⁵ to V⁺⁴ at the stage of alcohol adsorption. In this case, the carbon atom is oxidized, which corresponds to the general idea of its state in formaldehyde. Both the terminal and bridging oxygen of the cluster are converted into a hydroxy group, which is confirmed by the equalization of their charges.

According to simulation, CH₃OH oxidation to CH₂O on neutral V₄O₁₀ cluster requires the presence of different sites including V, O(b), O(t). The role of the two oxygens O(t) and O(b) is shown to be different. Bridging oxygen V–O–V is active in O–H bond cleavage, while terminal V=O is necessary for C–H bond cleavage in CH₃–. The methanol oxidation on the cluster is accompanied by a change in the electronic state of vanadium and two oxygen sites of the cluster, which causes high activation energy of the C–H bond cleavage. So, methanol oxidation on a model neutral V₄O₁₀ cluster is expected to occur only at elevated temperatures.

The potential applications and possible ways to improve V₄O₁₀ reactivity can be explored. Based on the ideas described in the review [4], the properties of transition metal oxide clusters are determined by the presence of mono-nuclear oxygen-centred radical species O^{–*} in their composition. To have oxygen-centred radical O^{–*}, the composition

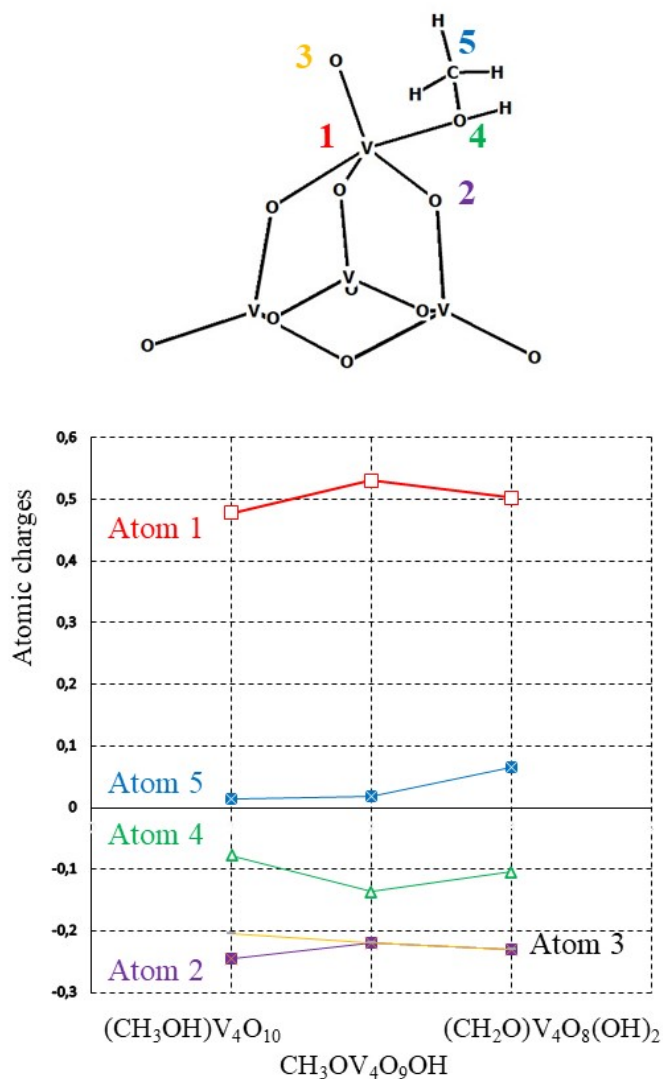


FIG. 3. Calculated atomic charges in the complexes involved in methanol oxidation on V_4O_{10}

of the oxide cluster $M_xO_y^q$ must satisfy the following formula:

$$\Delta = 2y - nx + q = 1,$$

in which n is the number of valence electrons of element M that can be oxidized by oxygen to $+n$ oxidation state. The Δ is called as *extent of cluster over-oxidation*. Substituting the charge and composition of our neutral V_4O_{10} into this formula leads to $\Delta = 0$:

$$\Delta = 2 \cdot 10 - 5 \cdot 4 + 0 = 0.$$

Thus, neutral V_4O_{10} does not contain oxygen radical species O^{-*} ; therefore, it is unreactive to oxidation. The situation can be corrected by changing the cluster's charge with saving atomic composition. When the charge is $+1$, the calculated extent of cluster over-oxidation is 1. So, cationic $V_4O_{10}^+$ contains an active oxygen radical, and it is expected to exhibit higher activity in the oxidation of methanol. Based on such reasoning, the catalytic properties of the cationic $V_4O_{10}^+$ cluster are tested in methanol oxidation. Anion $V_4O_{10}^-$ cluster is also considered for comparison.

Optimization of the structure of $V_4O_{10}^+$ and $V_4O_{10}^-$ estimated that, in general, they retain the structure of a neutral cluster with complete preservation of key distances in the case of an anionic cluster, and a slight reduction in the $V=O$ distance to 1.59 Å and an increase in the $V-O$ distance to 1.80 Å in the cationic one. Atomic charges in the charged clusters were calculated. The loss of one electron from a neutral cluster results in a decrease in charge on all atoms: V atom is $MS=1.1627$ or $HS=0.6304$; O(t) atoms are $MS=-0.2072$ or $HS=-0.0996$; O(b)* atoms are $MS=-0.4622$ or $HS=-0.1744$; O(b) atoms are $MS=-0.4745$ or $HS=-0.1939$. The spin density has the shape of a p orbital and is mainly localized at O(t) atom. A small amount of the spin density is also delocalized over the two closest O(b)* atom. For the anionic cluster, an alternative distribution of charge and electron density is observed: V atom is $MS=0.8959$ or $HS=0.4508$; O(t) atoms

are $MS = -0.3662$ or $HS = -0.2966$; O(b) atoms are $MS = -0.5097$ or $HS = -0.2650$. The spin density has the shape of a d orbital and is mainly localized at V atom.

Let us consider how the difference in the electronic structure of $V_4O_{10}^+$ and $V_4O_{10}^-$ will affect their reactivity in methanol oxidation. The structures and energies of the charged complexes involved in the stages of methanol oxidation to formaldehyde, which were determined for the neutral V_4O_{10} , were calculated and the energy changes in stages 1, 2 and 3 was estimated (Table 1). The anionic cluster activates methanol very poorly in the associative step. In the first stage, a $(CH_3OH)V_4O_{10}$ complex is formed with a binding energy lower than that of a neutral cluster. The cleavage of the O-H bond in the alcohol molecule is also less favorable than for neutral cluster. Thus, the $V_4O_{10}^-$ exhibits poor activity in preactivating even the O-H bond in methanol. Therefore, there is no point in studying its properties in C-H bond cleavage; its thermodynamic and kinetic properties in this case are obviously poor. In contrast, for the cationic $V_4O_{10}^+$, an increase in energy change is observed even at the first associative stage. Further O-H bond breaking (stage 2) is also energetically favorable. The largest energy change is calculated for C-H bond cleavage (stage 3) in the CH_3 -O-intermediate and the formation of formaldehyde.

TABLE 1. Calculated energy changes (kJ/mol) in stages 1, 2 and 3 of methanol oxidation on V_4O_{10} , $V_4O_{10}^+$, $V_4O_{10}^-$

Charge	ΔE_1	ΔE_2	ΔE_3
0	-59.3	-55.4	+130.0
+1	-142.4	-38.8	-112.8
-1	-30.0	-24.8	—

As noted earlier, stage 3 is the rate-determining step in methanol oxidation on vanadium oxide. To test its rate on the cationic $V_4O_{10}^+$ cluster, the transition state is found and the activation energy is calculated. The transition state structure is shown in Fig. 4. The calculated activation energy is 42.1 kJ/mol, indicating that formaldehyde forms on the cationic cluster at low temperature. Two possible reasons for the decrease in activation energy can be identified. The first is the presence of an oxygen radical within the cluster, which facilitates methanol activation. The second reason is the loosening of the stable tetrahedral structure due to the loss of one electron. This leads to the easy opening of the cage, which is necessary for the transition state of the third stage, leading to the cleavage of the C-H bond in the CH_3 -O intermediate.

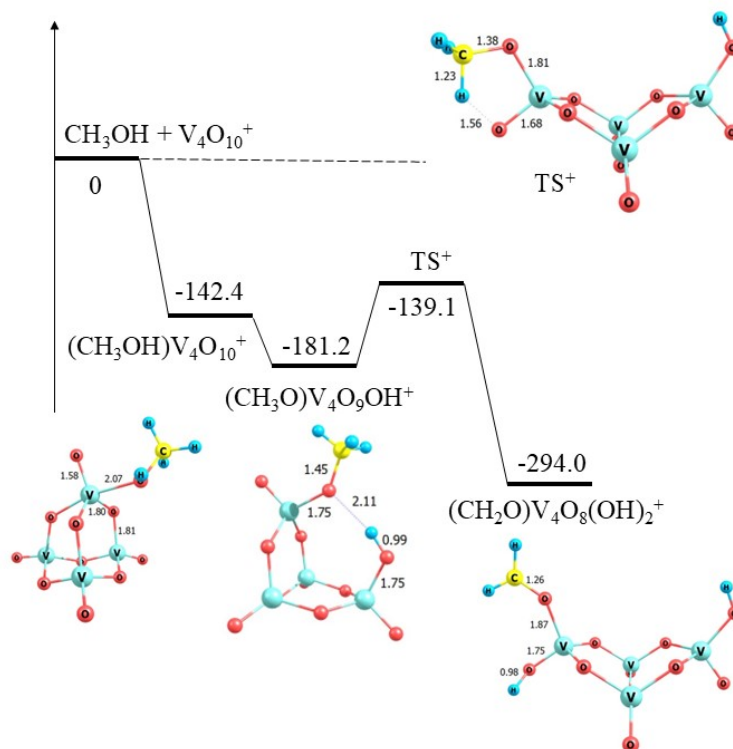


FIG. 4. An energy diagram illustrating the change in energy at the stages of methanol oxidation on $V_4O_{10}^+$ relative to the total energy of the cluster and methanol (energies are given in kJ/mol)

Can cationic clusters form on the surface of a heterogeneous catalyst? It is known that the support used to stabilize transition metal oxide nanoparticles can generate positively or negatively charged sites. Among the vanadium oxide catalysts considered in methanol oxidation, the most active one is $\text{V}_2\text{O}_5/\text{TiO}_2$ [22]. It can be assumed that titanium oxide creates cationic vanadium oxide. Alternatively, titanium itself can be part of the active site forming an active oxygen radical. Calculation of the expected composition of the bimetallic cluster according to the formula proposed in the review [4] leads to $\text{TiV}_3\text{O}_{10}$. Simulation of methanol oxidation on a mixed vanadium-titanium oxide cluster requires further investigation and will be addressed in the future work.

4. Conclusions

The present study provides a detailed quantum chemical analysis of methanol oxidation to formaldehyde on the model V_4O_{10} cluster using DFT methods. The results demonstrate that the reaction proceeds via a multistep mechanism involving methanol adsorption, O–H bond cleavage, and subsequent C–H bond activation, with the latter identified as the rate-determining step. It has been shown that the catalytic activity of the neutral V_4O_{10} cluster is limited by a high activation barrier for C–H bond cleavage, which restricts the reaction to elevated temperatures. The analysis of electronic structure and atomic charge redistribution reveals that both terminal and bridging oxygen atoms play distinct and essential roles in the reaction mechanism, with bridging oxygen sites facilitating O–H bond cleavage and terminal oxygen atoms participating in C–H activation.

A key finding of this work is the pronounced effect of cluster charge on catalytic performance. The introduction of a positive charge leads to the formation of oxygen radical species and significantly enhances catalytic activity. In particular, the cationic $\text{V}_4\text{O}_{10}^+$ cluster exhibits a substantially reduced activation energy for the rate-determining step, enabling methanol oxidation under milder conditions. In contrast, the anionic $\text{V}_4\text{O}_{10}^-$ cluster demonstrates poor reactivity, particularly at the initial activation stages.

These results highlight the importance of electronic structure tuning in transition metal oxide nanoclusters and suggest that cationic species may represent the true active sites in supported vanadium oxide catalysts. The findings also provide a theoretical basis for the design of more efficient catalytic systems, including mixed-metal oxide clusters such as Ti–V–O systems, which may further enhance reactivity through electronic and structural modification. Overall, this study contributes to a deeper understanding of the relationship between charge state, electronic structure, and catalytic activity in vanadium oxide nanoclusters, offering valuable insights for the rational design of catalysts for selective methanol oxidation.

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