

$V_2O_5^+$ reaction with C_2H_4 : theoretical considerations of experimental findings

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Abstract. Density functional calculations have been performed for the $V_2O_5^+$ reactions towards ethylene considering atomic and molecular oxygen loss, oxygen transfer and association reactions. The oxygen transfer channel to ethylene is energetically favourable in contrast to the oxygen loss. This is in agreement with the experimental results [1] which show that $V_2O_5^+$ does not lose atomic oxygen during the collision induced dissociation at thermal energies. A radical cation mechanism based on structure-reactivity relation of $V_2O_5^+$ cluster is proposed to explain oxygen transfer channel indicating that this reaction is size selective.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

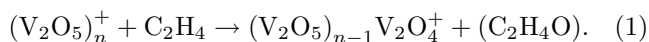
1 Introduction

The oxidation of organic molecules constitutes a major portion of catalytically generated products [2,3]. Vanadium oxides are among the most widely used group of industrial catalysts for the selective oxidation of hydrocarbons [4,6]. However, the mechanisms which govern these reactions are still not completely understood. As a result, there is a need to identify and characterize the active sites responsible for the reaction and any intermediates which may be involved in the mechanism. Studying the structure-reactivity relationship of heterogeneous catalysts provides valuable information on the active sites responsible for the reactions. Considering the variety of coordination sites present on the surfaces, current surface sensitive techniques are not capable of effectively characterizing these sites [7]. The surface of a metal oxide catalyst can be thought of as a collection of clusters of varying sizes and isomers [8]. Consequently, clusters share some characteristics with the surfaces of heterogeneous catalysts, including multi-site interactions and high ligand mobility [9]. These qualities make it feasible that clusters may act as models for the active sites on catalytic surfaces. In fact, Zamaraev and co-workers have found similarities in the products of gas phase reactions and those in the condensed phase [10]. Specifically, $Mo_3O_y^+$ clusters produce long chain hydrocarbons when reacted with several methanol molecules which is also observed in catalytic reactions. Muettertius reviewed the potential to use clusters

as simple models for the chemisorption and catalytic processes on the surfaces of heterogeneous catalysts, termed the “cluster surface analogy”. He pointed out that this area of research may yield vital information on the mechanisms of certain catalytic reactions [11]. Currently, several research groups are engaged in experimental as well as theoretical studies to further the fundamental knowledge of catalytic active sites through cluster research. The experiments conducted in the Castleman laboratory focus on ionic clusters which then enable mass selection. The literature has shown an interest in modeling surfaces using cationic and anionic clusters [12,15]. Experimentally, Yates *et al.* have found that oxygen vacancies produced during the annealing process are essential for the photooxidation of CH_3Cl on TiO_2 (110) surface [12]. Additionally, charge sensitivity analysis (CSA) combined with the semiempirical methods for electronic structure calculations has been used to demonstrate that clusters can serve as suitable models of catalytically active sites. Nalewajski and Korchowiec used CSA to show that oxygen and vanadium atoms in V_2O_5 surface clusters act as local basic and acidic sites, respectively [13]. Experimental studies on the reactions between Group V metal oxide cluster ions and the C2 hydrocarbons, ethane and ethylene [1] showed a remarkable phenomenon occurred during the reactions between $(V_2O_5)_n^+$ and the C2 hydrocarbons. A significant oxygen loss pathway was observed for $V_2O_5^+$, $V_4O_{10}^+$ and $V_6O_{15}^+$ at thermal energies. It was suggested to be an oxygen transfer process shown in the reaction below rather than oxygen loss as confirmed by previously conducted

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collision induced dissociation (CID) studies [16]



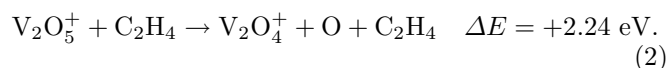
The CID results showed that the $(\text{V}_2\text{O}_5)_n^+$ clusters do not exhibit an oxygen loss reaction pathway at thermal energies, the same conditions under which the reactions with the C2 hydrocarbons were performed. However, since neutral species cannot be experimentally identified oxygen transfer to the hydrocarbon could not be proved. Therefore, the theoretical work based on density functional calculations has been initiated in order to determine energetics and to propose mechanisms responsible for different reaction channels.

2 Computational methods

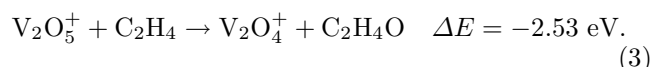
In this contribution the calculations were carried out at the density functional level of theory using the Becke's hybrid three parameter nonlocal exchange functional combined with the Lee-Yang-Parr gradient corrected correlation functional (B3LYP) [17] and employing the all-electron triple- ζ valence plus polarization basis set (TZVP) developed by Ahlrichs and co-workers [18]. It has been shown that this approach yields adequate description of the structural properties and energetics of neutral and anionic vanadium oxide clusters [19]. In addition, the accuracy of the method for cationic vanadium oxide clusters was checked by calculating dissociation energies for VO^+ and VO_2^+ . The calculated dissociation energy for VO^+ is 3.80 eV which compares well with the experimental value of $D_e = 3.51 \pm 0.36$ eV [20] considering the large error bars. The dissociation energy for $\text{VO}_2^+ \rightarrow \text{VO}^+ + \text{O}$ is 5.52 eV which is somewhat lower than the experimental value of dissociation threshold which includes also the barrier $D_e = 6.09 \pm 0.28$ eV [20]. Therefore, the difference between these two values is acceptable. The calculations were carried out using Gaussian [21] and Turbomole [22] programs. All structures were fully optimized employing gradient-based energy minimization methods and the stationary points were characterized using vibrational frequency analysis. In order to study the mechanism of the oxygen transfer reaction from V_2O_5^+ to ethylene, transition state structures (TS) corresponding to the involved reaction steps have been optimized using the synchronous transit guided quasi-Newton (STQN) method developed by Schlegel and co-workers [23] and barriers for the reaction steps were determined. In order to confirm the proposed mechanism for the oxygen transfer reaction, additional *ab initio* molecular dynamics (MD) with forces calculated using RI-DFT procedure [24] with the BLYP functionals were carried out. The activated complex of V_2O_5^+ cluster and ethylene was used to initiate the MD simulations. For this purpose initial velocities were generated by randomly distributing the energy corresponding to the stability of the complex among all internal degrees of freedom. Such MD simulations allowed us to follow the reaction mechanism, and to verify the intermediates and reaction steps which are involved in the mechanism responsible for the oxygen transfer.

3 Results and discussion

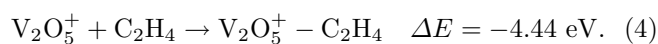
The structure of V_2O_5^+ was calculated to be an oxygen centered radical species with the two vanadium atoms joined by doubly bridged oxygen atoms in agreement with the literature [25,26]. The calculated energy for the single oxygen loss from V_2O_5^+ shows that a simple collision induced loss process is thermodynamically unfavorable with an energy of +2.24 eV as shown in the reaction below



However, the V_2O_5^+ does yield a V_2O_4^+ product during the reactions and the structural properties do show that one oxygen atom is bound less strongly to vanadium in V_2O_5^+ , which is not observed in the V_2O_4^+ and V_2O_6^+ clusters. Hence, it was concluded that CID oxygen loss was improbable for the collision processes with ethane and ethylene since the CID studies, mentioned earlier, showed no atomic oxygen loss at thermal energies but only upon the addition of 0.08 mtorr Kr and an excess energy of collision of 1 eV, center-of-mass energy [16]. In addition, the calculations presented here support this conclusion, requiring 2.24 eV of energy to cleave the V-O bond for the oxygen loss reaction. Therefore, it was concluded that the reaction must occur *via* another mechanism. The most probable process is one involving an oxygen transfer reaction channel illustrated in reaction (3) below



The reaction pathway for this oxygen transfer reaction is shown in detail in an energetic profile in Figure 1. The figure illustrates that the proposed pathway involving the oxygen transfer reaction is the most likely to occur during the experiment. The first step involves the association of the ethylene molecule to the cluster. For the V_2O_5^+ cluster, this occurs with the ethylene bound to both terminal oxygen atoms. One of the C-O bonds is then cleaved, with a transition state of 1.45 eV higher in energy than the association complex. A hydrogen atom is then transferred from the carbon atom bound to the oxygen atom to the second carbon atom, which is energetically lower than the association complex by 0.75 eV shown in Figure 1 as the second local minimum. Finally, the V-O bond is broken producing acetaldehyde ($\text{C}_2\text{H}_4\text{O}$) and V_2O_4^+ , experimentally observed as the dominant product for the reaction between V_2O_5^+ and ethylene. The energy calculated to form the association product is -3.53 eV for the ethylene bound to one terminal oxygen atom (*cf.* Fig. 2) and -4.44 eV for the ethylene bound to the two terminal oxygen atoms in the V_2O_5^+ structure, (*cf.* Fig. 3). The reaction to form the association product of V_2O_5^+ is shown below



This association product is the most stable pathway open to V_2O_5^+ and yet is only weakly observed during the experiment. Hence, the bimolecular reaction occurs due to

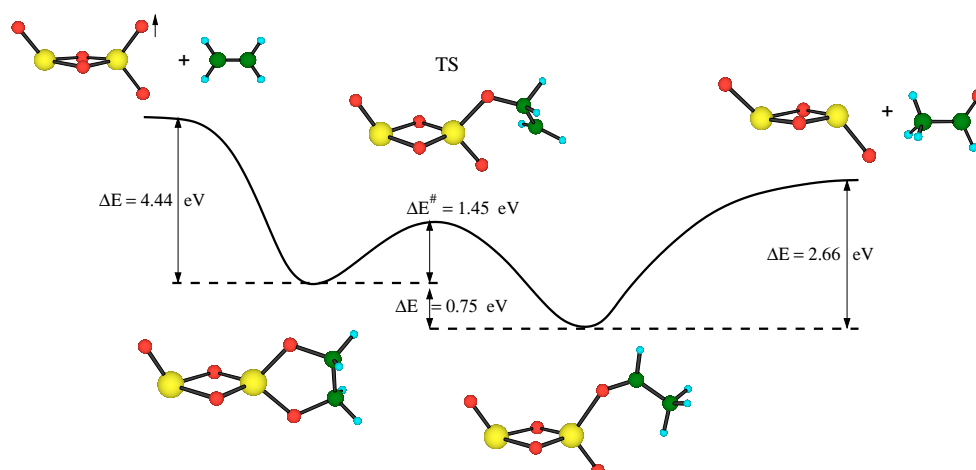


Fig. 1. Energetic profile for the oxygen transfer reaction from $V_2O_5^+$ to ethylene.

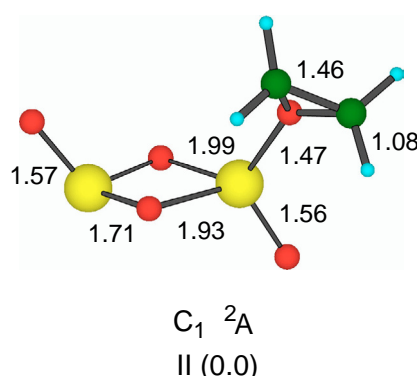
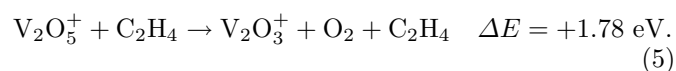


Fig. 2. The structure of the association product of $V_2O_5^+$ with ethylene. Ethylene is bound to one oxygen atom.

the significant amount of energy the complex retains after this reaction, thereby requiring a third-body collision for energy removal and stabilization. However, some fraction of the complexes remains intact throughout the course of the experiment, since the association product of $V_2O_5^+$ is weakly observed. The energy gained from the formation of the association complex can also be released through a bimolecular reaction pathway. This is likely to follow the mechanism for oxygen transfer described above and is the most likely outcome. Another possibility is that both V-O bonds attached to the ethylene might be broken (*cf.* Fig. 3). This yields the ethene-diol or two formaldehyde molecules as proposed below for the possible reaction pathway resulting in the loss of two oxygen atoms from the $V_2O_5^+$ cluster (*cf.* reactions (6) and (7)). The energy for the molecular oxygen loss pathway was calculated to be an endothermic process shown in the following:



This product, $V_2O_3^+$, is observed experimentally and therefore, there must be an alternate mechanism to simple O_2 loss to explain the results. In addition, during CID experiments, O_2 is lost from $V_2O_5^+$ however, this only oc-

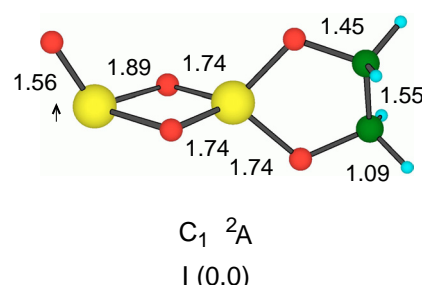
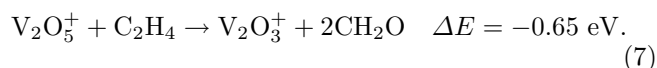
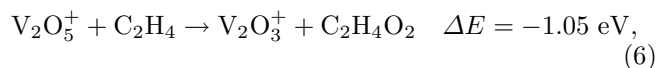


Fig. 3. The structure of the association product of $V_2O_5^+$ with ethylene. Ethylene is bound to two oxygen atom.

cur at center-of-mass energies in excess of 2 eV. The reactions between the $V_xO_y^+$ clusters and ethylene were conducted under thermal conditions and therefore the energy necessary to lose molecular oxygen from $V_2O_5^+$ was not available to the cluster. Therefore, the reaction must occur through another mechanism, most probably by reacting with the ethylene and forming ethene-diol or two formaldehyde molecules illustrated below in reactions (6) and (7) respectively



Both reactions are overall energetically favourable and the reaction most likely follows the path to forming the two formaldehyde molecules probably due to a high-energy barrier, which must be overcome, for the ethene-diol formation to occur. In fact the latter reaction should involve the transfer of two hydrogen atoms and breaking of two V-O bonds which is highly improbable due to expected high energy barriers. Moreover ab initio MD simulations carried out to verify proposed reaction pathways showed that the reaction (7) involving the formation of two formaldehyde molecules is more likely to occur. However, this requires a high excess of energy and therefore the yield of

this reaction should be considerably lower than that of oxygen transfer to ethylene.

The results noted experimentally are well explained by the theoretical calculations. Although association is energetically the most favourable pathway, the observation of the channels for oxygen transfer and formaldehyde formation is justified. In fact, the radical cation mechanism proposed for oxygen transfer to the ethylene based on the structure-reactivity relationship for $V_2O_5^+$ clarifies the dominance of this reaction channel in the experiment. Further calculations are currently being performed to explain the reaction pathways of additional vanadium oxide cluster cations with the C2 hydrocarbons.

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