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A DFT study of oxidative dehydrogenation of ethyl benzene to styrene over zirconium vanadate catalyst

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ABSTRACT

A DFT modeling of the transition state of oxidative dehydrogenation of ethylbenzene over zirconium vanadate catalyst has been carried out. Computations confirm a Mars-Van-Krevelen type redox mechanism in which the catalyst abstracts a hydrogen atom from the hydrocarbon and catalyst is reduced. The reduced catalyst is re-oxidized by oxygen from air. Computations suggest the formation of a hydroxyl species over the catalyst surface believed to have been formed due to abstraction of hydrogen atoms from ethyl benzene. A cyclic intermediate is formed which easily accepts one oxygen atom from air to regenerate the catalyst. The study shows that active species is vanadium and it follow a redox order of V=+5, V=+4, V=+3, V=+5.

Keywords: ODH, Zirconium Vanadate, Reaction Mechanism, Ethyl Benzene, Styrene, Transition State.

INTRODUCTION

Oxidative dehydrogenation (ODH) of saturated hydrocarbons to produce unsaturated hydrocarbons is of great importance because of commercial usefulness of unsaturated hydrocarbons and their derivatives such as epoxides [1]. ODH of ethyl benzene (EB) produces styrene (S) which can be easily oxidized to styrene oxide, both being monomers for polystyrene/polystyrene oxide [2]. Styrene oxide can be further reduced to 2-phenyl ethanol and can even be reacted with CO_2 to produce polycarbonates [3]. Conventional methods for the production of styrene involve dehydrogenation of ethyl benzene over various catalysts [4-6]. Recent researches have shown that V_2O_5 catalyst is a better alternative for ODH compared to the traditional ferrite catalysts as the reaction over this catalyst is exothermic and performs at lower temperature and results in higher yield of styrene [7]. Besides, the heat generate during operation can be utilized for steam /electricity generation.

Activated carbon [8], CeO_2 [9], activated carbon from natural source [10], VO_x/Al_2O_3[11], vanadia incorporated titania [12], vanadia supported over antimony oxide[13], have been used as catalyst for ODH of ethyl benzene to styrene.

Air [9], O_2/N_2 mixture [10], N_2O [11], O_2 [12], CO_2 [13] has been used as oxidants for regeneration of the catalyst. Styrene yield as high as 85% is reported by Jie Xu *et al.*[9] and Gopinath *et al*[12]. Al_2O_3, TiO_2, SiO_2, ZrO_2, MgO, and HfO_2 [14-18] have been used as support for vanadia. Among these ZrO_2 is best because of its chemical and thermal stability, strong support – catalyst interaction and high dispersion [19].

Raju *et.al* [20] has studied the oxidative dehydrogenation of ethyl benzene and n-butane over $TiO_2{-}ZrO_2$ (TZ) mixed oxide-supported V_2O_5, CeO_2 and V_2O_5–CeO_2 catalysts. $V_2O_5{-}CeO_2/TiO_2{-}ZrO_2$ catalyst exhibited high performance for ODH of ethylbenzene and $V_2O_5/SnO_2{-}ZrO_2$ catalyst was found to exhibits good performance for ODH of n-butane.

Shah *et.al* [21] studied a number of industrial oxidation reactions over vanadia supported on a variety of supports such as ceria, alumina and ZrO_2 and found that strength of oxygen binding in these catalyst is affected by the support due to the formation of mixed oxide compounds such as $CeVO_4$, ZrV_2O_7, and $AlVO_4$ at the interface between support and active component during calcinations.

Most of the mechanisms proposed for oxidation, ammoxidation and oxidative dehydrogenation of alkyl aromatics are based on Mars-Van-Krevelen type redox mechanism [22]. Supports in the favour of this mechanism are traditional kinetics studies of the reactions by fitting rate data into the model. Few publications support this mechanism by Temperature-programmed reduction (TPR) and Transmission Electron Microscopy (TEM) measurements also [23, 24]. In recent years density functional theory has been applied to glean information of the mechanism the reaction [25, 26]. To the best of our knowledge there is no report on the mechanism of ODH of ethylbenzene based on DFT Theory. The present problem of the DFT study of ethylbenzene over zirconium vanadate was therefore undertaken to (1) understand the mechanism of hydrogen abstraction from hydrocarbon (2) know the structure of TS structure (3) estimate of activation energies of different steps and (4) elucidation of the reaction pathways.

MATERIALS AND METHODS

All the DFT calculations for the current problem were performed using Gaussian 09W suite [27]. The B3LYP functionals were used to describe electron exchange and correlation [28], while Lanl2dz basis set was used to find the optimized geometries of reactants, products, and transition state. For transition state calculation QST2/QST3 keyword has been used [29]. At many places the optimization of transition state was achieved directly also [30]. Many times optimized geometries are still not good enough to predict the transition state geometry. In these cases, various techniques such as Potential Surface Scan and Linear Synchronous Transit (LST) method can be applied to get closer to a transition state. Vibrational frequencies were calculated for the optimized geometries to identify the nature of the reactant or product (no imaginary frequency) and TS structure (one imaginary frequency).

The enthalpy and the activation energies were calculated at the reaction temperature as described by J.W Ochterski [31].

Convergence has been considered to be achieved when forces on the atoms become less than the cutoff value. The adsorption energy (E_{ads}) was calculated as [32, 33]

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

Geometry optimization for all the structures was done. The results indicated that the optimized distances and angles in the model were in good agreement with the experimental values [34]. A preliminary report for the catalyst synthesis and process optimization has been published [35].

RESULTS AND DISCUSSION

The catalyst structure and its optimization.

We had optimized the representative model of the catalyst. The model has been created assuming an octahedral environment for zirconium and tetrahedral environment for vanadium. In the actual structure of zirconium vanadate, the vanadium atom present in tetrahedral environment and zirconium present in octahedral environment [34]. The remaining valancies were satisfied with hydrogen atom to reduce the number dangeling bonds.The structure for model catalyst is shown in Fig.1. The bond lengths V=O (vanadyl group), V-O bridging viz, $V\text{-}O_{Zr}$ and $V\text{-}O_V$ were calculated to be 1.59 Å, 1.70Å and 1.77 Å respectively which compare well with the reported values of 1.66 Å, 1.68 Å and 1.75 Å [30]. The calculated bond length for Zr-O was 2.08Å (Exp-2.06 Å) while the V-O-V and Zr-O-V bond angles were 165.8° (Exp-166.2°) and 153.4° (Exp-154.7°) respectively [30]. Most of the mechanisms suggested for oxidative dehydrogenation of organic compounds by air over supported vanadium catalysts are based on Mars-van Krevelen redox mechanism [22] and the C-H bond activation step is the rate determining step [23]. According to this mechanism the V_2O_5 catalyst is first reduced by the hydrocarbon and is then subsequently re-oxidized by the di-oxygen of air.

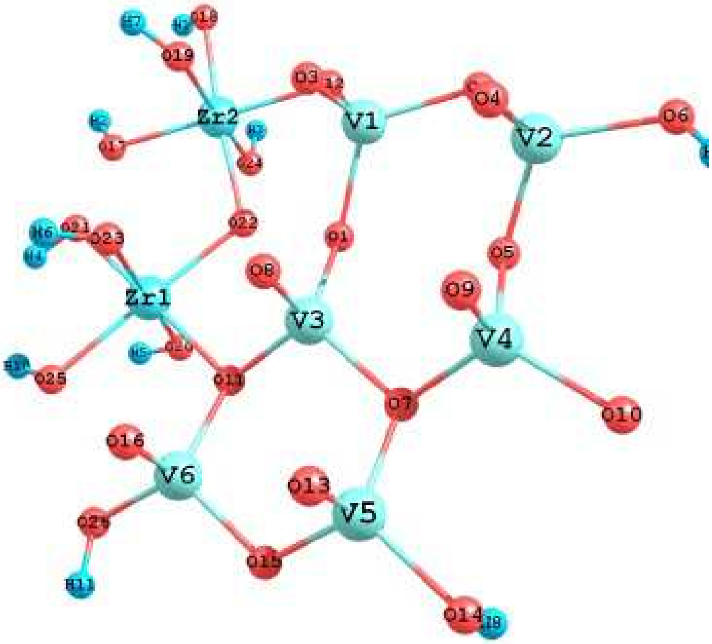


Fig.1 Optimised Structure of the Catalyst

Molecular adsorption of ethyl benzene:

In ZrV_2O_7, we can distinguish three types of oxygen atoms namely, vanadyl oxygen (O1), bridging oxygen atom (O2) V-O-V or V-O-Zr and triply coordinated oxygen atom(O3). DFT calculations were performed for adsorption of EB at all of these oxygen atom sites. The calculated heats of adsorption at O1, O2 and O3 are 4.2, 14.5 and 22.5 Kcal/mol respectively. The positive adsorption energies can be attributed to DFT calculation to take into account the electrostatic interaction part of van der Waal interactions leading to underestimation of physisorption energy. Low values of heat of adsorption rule out role of physical adsorption in activation of C-H bond and suggest need for high temp chemisorptions for its activation. The minimum heat of adsorption was found at O1 which has highest nucleophilicity. For calculation at O1 and O2 sites we considered the catalyst as molecule while for O3 calculation we had consider a large cluster.

Activation of C-H bond:-

Absence of strong acidic or basic site at the catalyst, rules out the possibility of reaction to proceeding via acidic or basic mechanism and thus suggesting a non-ionic or free radical mechanism for the reaction. The previous DFT computations on ODH of alkanes suggest the abstraction of a hydrogen atom by the catalyst to be slow and rate determining step [36]. It has also been reported that H atom from methylene group is more prone to abstraction compared to that from methyl group due to higher bond enthalpy [36]. In the present case C-H bond abstraction is possible from methyl as well as methylene groups of EB. The support in favour of H abstraction from methylene group is the higher stability of the resulting radical (a secondary radical) as compared to that resulting due H abstraction from methyl group (a primary radical). The PES diagram for H atom abstraction from methyl and methylene groups is shown in Fig.2. The activation energy for methylene H abstraction is 83.3 kcal/mol while from methyl group it is 98.8 kcal/mol. This result also confirms the first H atom removal takes place from methylene group producing an oxyethylbenzene group and this step seems to be the rate determining step.

The TS structures for both possibilities are shown in Fig.3a and 3b. The C-H and O-H bond lengths in TS structure (Fig.3b) found to be 1.45 Å and 1.29Å respectively which are longer than respective normal bond lengths. The TS structure for H abstraction from methyl group the C-H and O-H bond lengths are 1.9 Å and 1.7 Å respectively Fig3a.

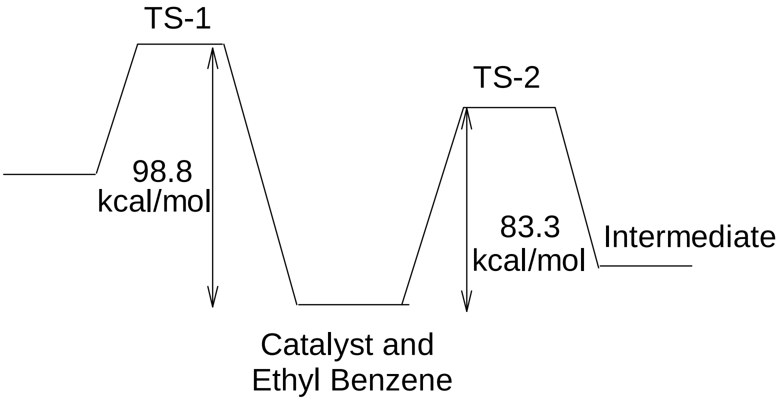


Fig.2 PES Diagram for H abstraction from methyl or methylene group

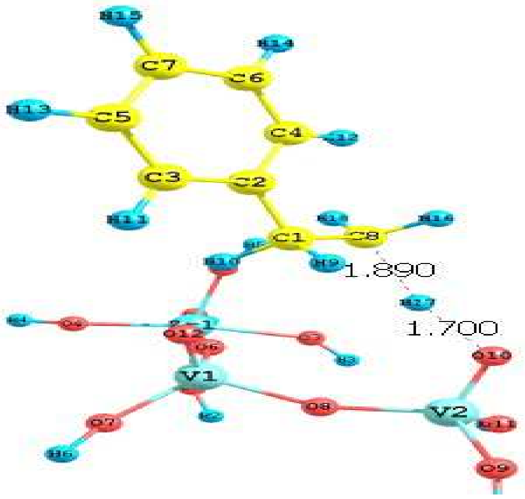


Fig.3a Transition state model showing H abstraction from methyl group

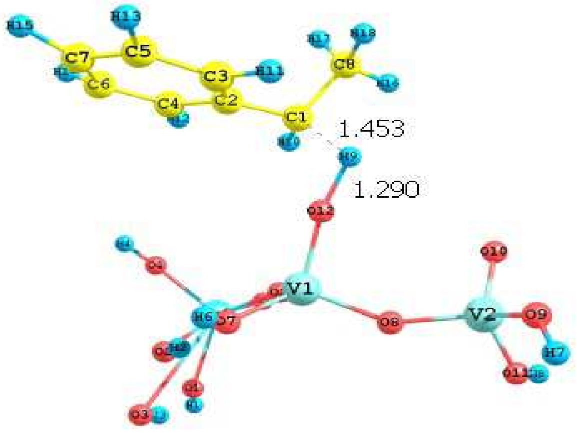


Fig.3b Transition state model showing H abstraction from methylene group

The structure of intermediate formed by H removal (oxyethylbenzene) is shown in Fig.4. The O-H bond length of 1.01 A in the intermediate is very close to the normal bond length in alcohols.

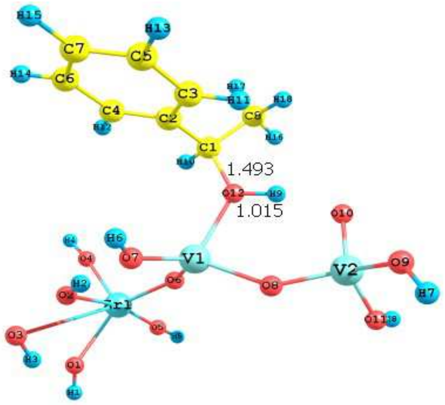


Fig.4 Structure of intermediate along with bond lengths

The activation energies for H abstraction from O1 and O2 sites were found to be 83.3 and 113.9 kcal/mol respectively suggesting higher possibility of H abstraction from O1 site compared to O2 site. The TS structure for removal H atom from O2 site is shown in Fig.5.

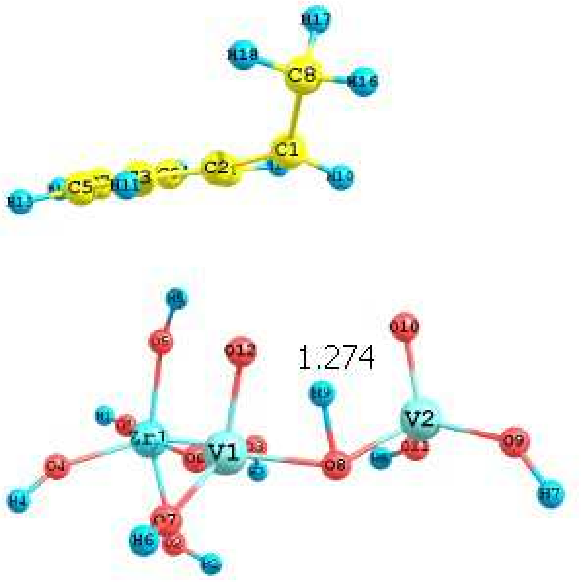


Fig.5. H abstraction from O2 site

The calculation of H abstraction at O3 site is not considered due to high steric constrain and high heat of adsorption. After H abstraction, ethyl benzene may form oxyethylbenzene intermediate or secondary ethyl benzene radical. The former may be termed as insertion mechanism while latter may be called radical mechanism and both involve the O1 site. The second H removal from methyl group to produce styrene may be from O1 itself or by nearby O1, O2 or O3 sites. On the basis of oxygen sites involved in the hydrogen(s) abstraction, we can describe the whole mechanism into three categories.

Mechanism involving O1 site
Mechanism involving O2 site
Mechanism involving O3 site

Mechanism Involving O1 Site- It may be categorized into insertion and radical mechanisms. In insertion mechanism the methylene C-H bond is activated at O1 site forming two new bonds namely C-O and O-H leading to the formation of an alcohol like species. The formation of similar species has also been reported by Fu *et.al* [32] also. The activation energy of the formation of the intermediate oxyethylbenzene is 83.3 kcal/mol and the translational frequency is at 1300.1*i* cm^{-1}. The structure of the intermediate is shown in Fig.4. Now the abstracted H atom gets transferred to nearby vanadyl oxygen atom with very low activation energy of 11.4 kcal/mol. The geometry of transition state is shown in Fig.6a. The imaginary frequency for the TS is 1438.2*i* cm^{-1}. The geometry of intermediate formed by transfer of H atom is shown in Fig.6b.

The second H atom removal from methyl group, leading to formation of styrene, may have four possibilities *i.e* by the same O1 atom (Bonded with Carbon), by the O1 atom (Hydroxyl Group), bridging oxygen O2, or O3 atom. The second H abstraction by O2 or O3 will be discussed later.

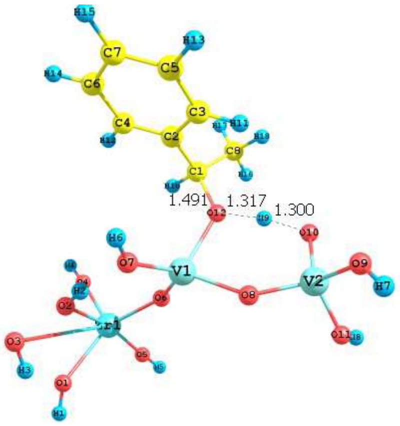


Fig.6a. Geometry of transition state for transfer of hydrogen atom to the neighboring vanadyl oxygen

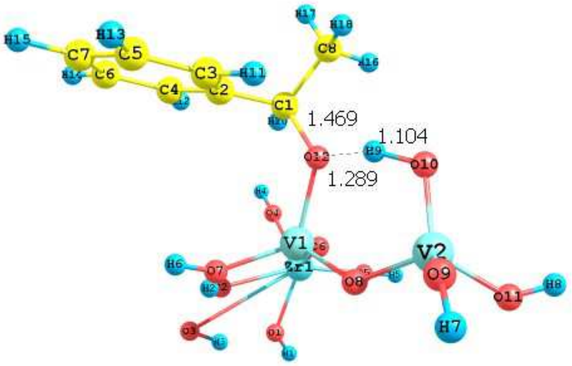


Fig.6b. Geometry of intermediate formed by transfer of H atom to the neiboring vanadyl oxygen

If methyl H abstraction occurs by its interaction with O1 of VOH moiety the formation of styrene and water molecules takes place which later on get desorbed and give rise to a vacancy at vanadium site. The TS has been calculated and the activation energy was found 162.3 kcal/mol with a translational frequency at 2096.3*i*cm^{-1}. The TS structure is shown in Fig.7a. The high activation energy associated with this path reduces its possibility.

If methyl H atom is removed by O1 bonded to the methylene carbon atom the activation energy for this step is also very high, 134.1 kcal/mol with imaginary frequency of 1760.4*i* cm^{-1}. TS is featured by lengthening of C-H bond of methyl group and get closer to oxygen atom along the lengthening of C-O bond leading to the formation of styrene. The TS structure for this possibility is shown in Fig.7b.

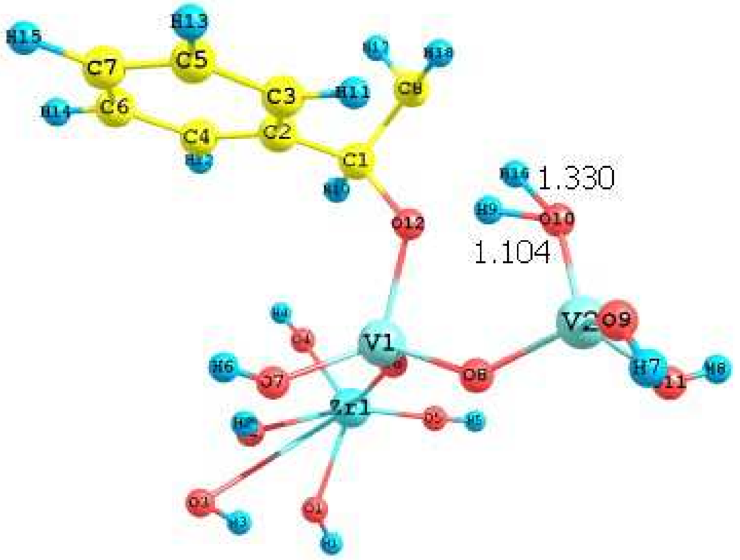


Fig.7a. TS Structure of methyl H abstraction by O1(Hydroxyl Group)

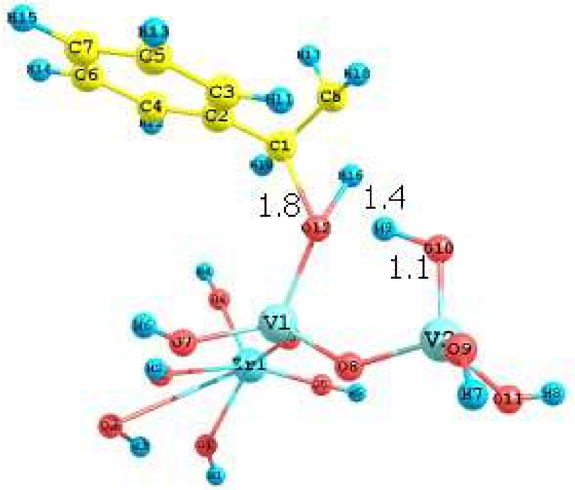


Fig.7b. TS Structure of methyl H abstraction by O1(Bonded With Carbon)

Radical Mechanism

In this mechanism first a methylene H is removed as a radical leading to the formation of secondary ethyl benzene radical. The TS structure for this step is shown in Fig.8. The imaginary frequency is -1412.5*i* cm^{-}1. The activation energy for this step is 57.2 kcal/mol and the O-H bond distance is 1.2 Å. Similarly, C-H and V=O bond lengths gets elongated from 1.09 Å and 1.59 Å to 1.55 Å and 1.79 Å respectively. The transfer of methylene H to vanadyl oxygen atom (O1) is of translational in nature as the corresponding frequency is calculated to be imaginary. Now the second H abstraction from methyl group is possible by vanadyl oxygen (O1) or by hydroxyl group. The transition state for both possibilities have been calculated and it was found that activation energy for abstraction of H by vanadyl oxygen atom is 28.3 kcal/mol while the same for hydroxyl oxygen is 70.11 kcal/mol. The H abstraction path by vanadyl group is preferred as it is of lower activation energy. In the TS showing the removal of H atom by vanadyl oxygen atom, the C-H bond length of methyl group gets elongated from 1.09.Å to 1.42 Å and the C-C bond length for ethyl group moiety shorten from 1.51Å to 1.41 Å showing formation of partial double bond between the two carbon atoms.

The Transition state for H removal from methyl group by hydroxyl .oxygen atom also shows elongation in C-H bond length of methyl group by 0.36Å and shortening of C-C bond length by 0.13Å. The activation energy for this step is 134.2 kcal/mol. The TS structure for both the processes are shown in Fig.9.

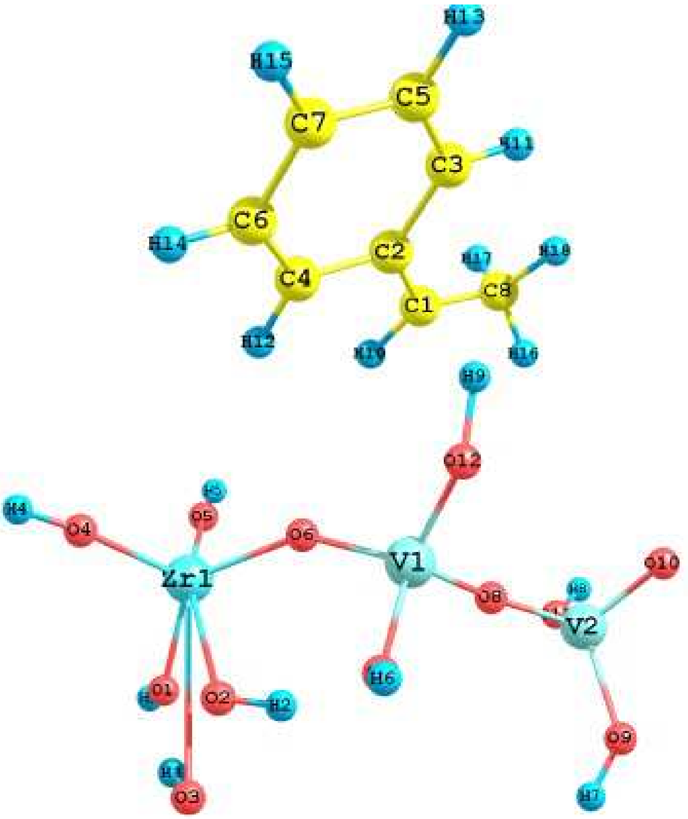


Fig.8. TS for methylene H abstraction as radical

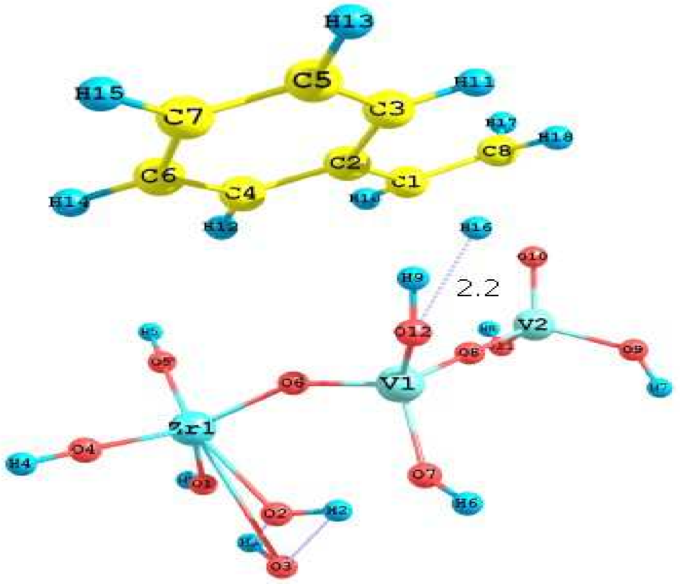


Fig.9a. TS Structure of methyl H abstraction by O1(Hydroxyl Group)

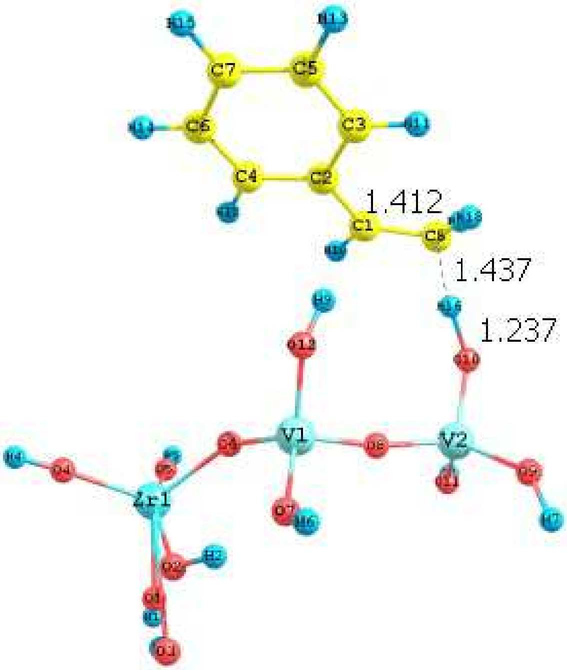


Fig.9b. Methyl H abstruction by O1 atom

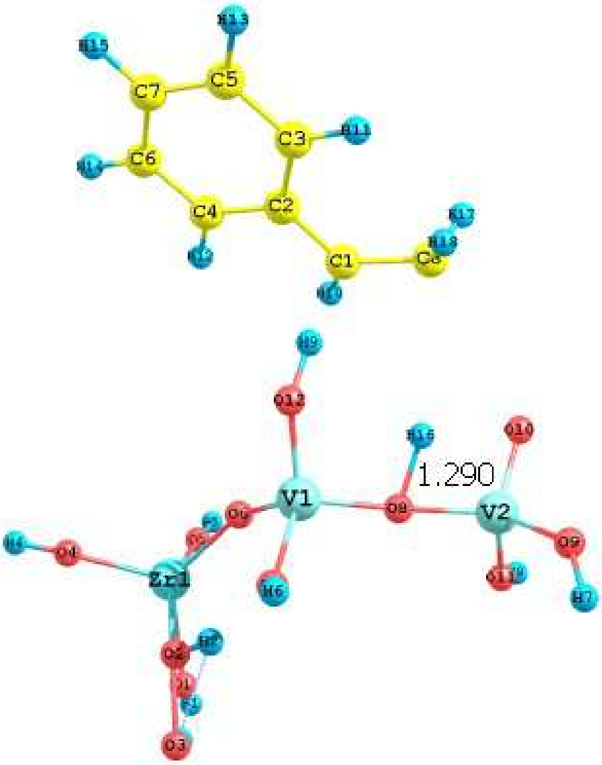


Fig. 10a. TS Geometry for methyl H abstraction by O2 from radical

Mechanism involving O2 atom- This mechanism involves possibility of second H removal from the radical or intermediate formed during methylene H abstraction by bridging oxygen (O2). The TS structure for second H removal from radical is shown in Fig.10a. This structure reveals the formation of hydroxyl group of bridging oxygen atom with bond length of 1.3 Å while the activation energy is exceptionally high (134.3 kcal/mol).

The activation energy computed for second H atom abstraction from intermediate by O2 is very low *i.e.*18.3 kcal/mol making it most feasible pathway. The TS structure is shown in Fig.10b.

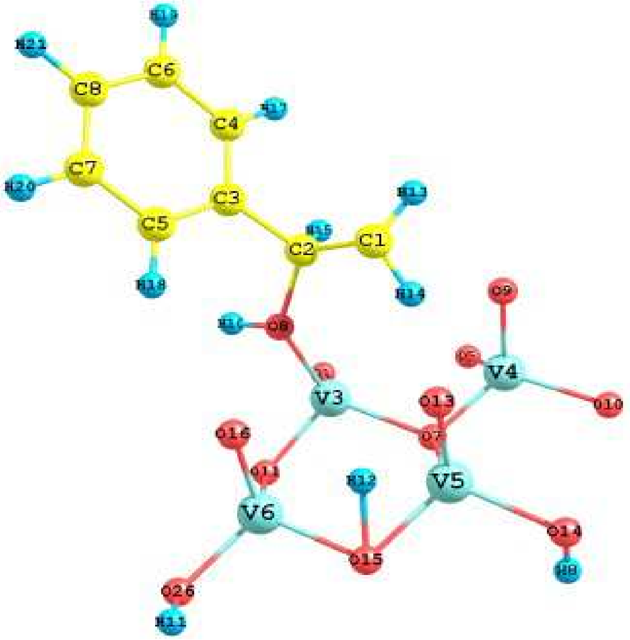


Fig. 10b. TS Geometry for methyl H abstraction by O2 from intermediate

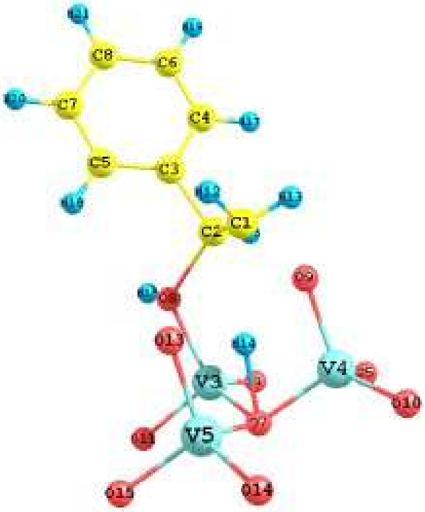
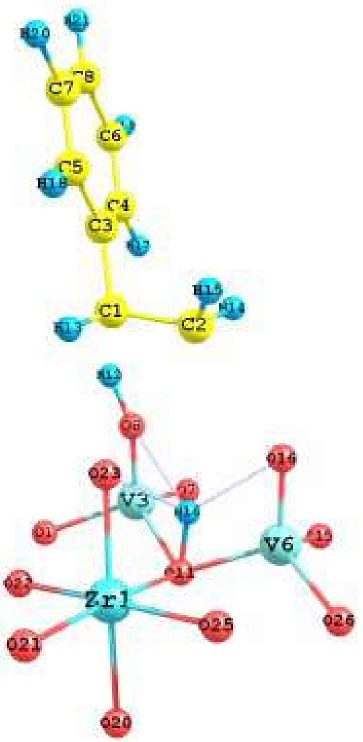


Fig.11.a. TS Structure for methyl H abstraction by O3 from intermediate

Mechanism involving O3 atom: This oxygen is triply coordinated and bonded to the three nearby vanadium atoms. This oxygen atom is least nucleophilic in nature and hence less reactive towards H abstraction [32]. The activation energy for H atom abstraction from intermediate by O3 is found to 28.3 kcal/mol which is higher than that by O2 site. The TS geometry is presented in Fig.11.a. The activation energy for the same process in case of radical was found to be 147.0 kcal/mol and the TS geometry is shown Fig.11.b.



11.b. TS Structure for methyl H abstraction by O3 from intermediate

Formation and desorption of product from reaction site:

From the aforesaid discussion it can be concluded that process of oxidative dehydrogenation of ethylbenzene starts with a methylene H abstraction from O1 site producing either a free radical or an oxyethylbenzene type intermediate. The free radical as well as the intermediate can further loose a hydrogen atom from the methyl group with the help of O1, O2 or O3 vanadium oxygen to produce styrene.

There are four pathways for methyl H abstraction from intermediate namely Path-A, Path-B, Path-C and Path-D as shown in Fig.12. The respective activation energies are 134.4 kcal/mol, 164.2 kcal/mol, 18.3 kcal/mol and 28.3 kcal/mol for paths A, B, C, and D respectively.

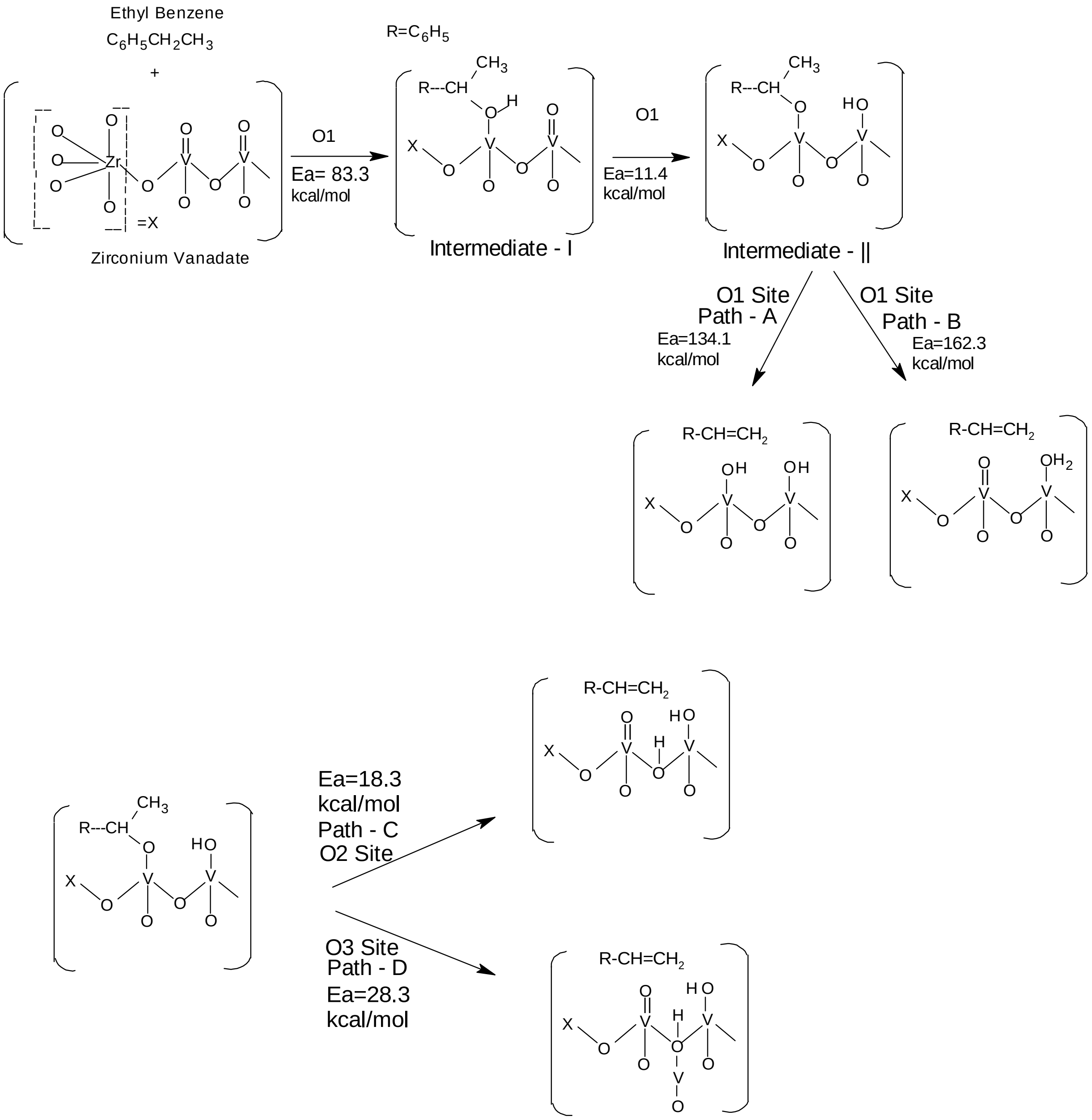


Fig 12. Possible routes emerging from intermediate for producing styrene

There are four pathways for methyl H abstraction in radical mechanism namely Path-E, Path-F, Path-G, Path-H as shown in Fig.13. The activation energies are 28.3 kcal/mol, 70.1 kcal/mol, 132.9 kcal/mol and 147.0 kcal/mol for Path E, F, G, and H respectively. It was also found that, the styrene desorption is endothermic process with ΔH of 12.2 kcal/mol.

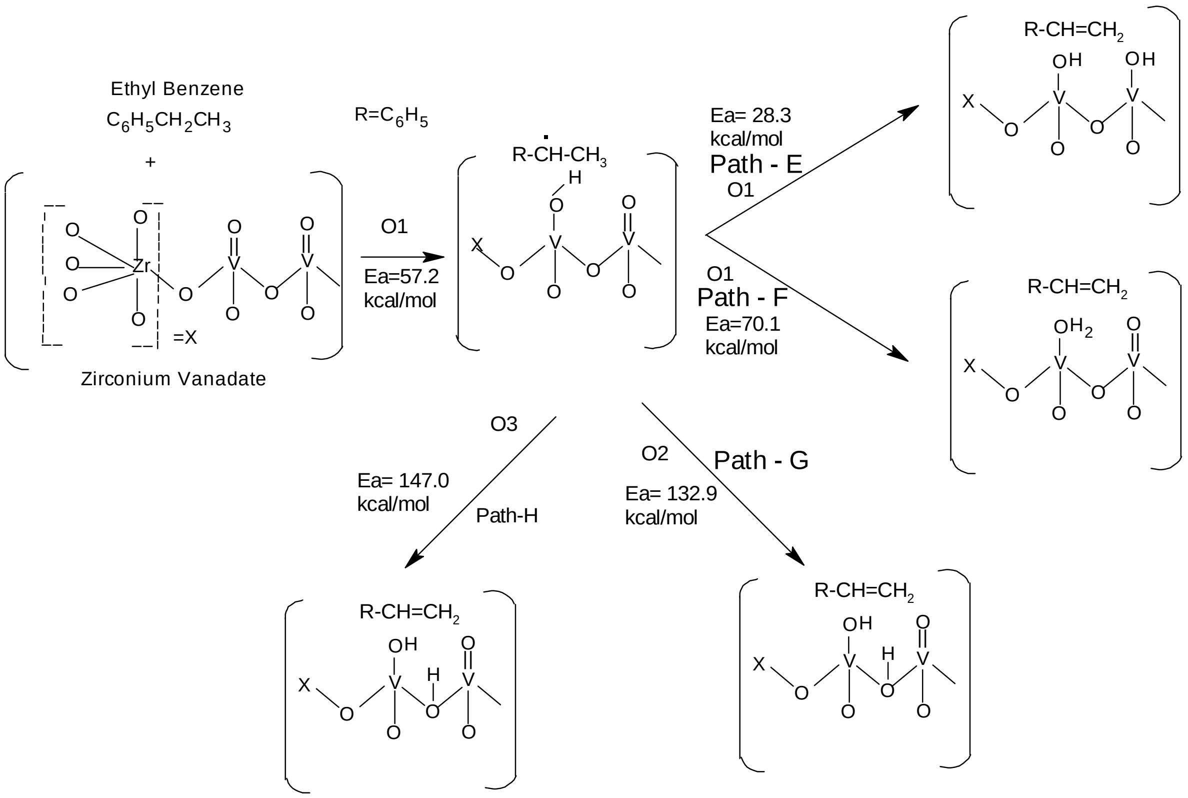


Fig 13. Possible routes emerging from radical for producing styrene

Catalyst Regeneration: After the product formation either a vacant site or a diol like species is formed. The diol like species eliminates a water molecule and produces a bridge like structure. This bridge like structure is converted into two separate vanadyl groups by taking one oxygen atom from oxygen of air during the catalyst regeneration step of the reaction At the surface of the catalyst the vacant site remains no more vacant for long time and it form a cyclic bridge like structure by making the bond with nearby O1 atom.

CONCLUSION

Mechanism of oxidative dehydrogenation of ethyl benzene to styrene over ZrV_2O_7 catalyst has been explained with the help of density functional theory calculations. It has been concluded that the reaction starts with the abstraction of a methylene hydrogen by vanadyl oxygen giving rise to oxyethyl benzene type intermediate or secondary ethyl benzene radical. The intermediate as well as radical can further loose methyl hydrogen with the help of vanadyl oxygen, bridge oxygen or triply coordinated oxygen to produce styrene. The minimum energy path for second H abstraction is computed to be path C. Geometry of all the transition states along with activation energy is reported.

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