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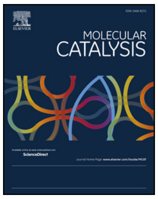

A DFT mechanistic study of the ODH of *n*-hexane over isolated H_3VO_4

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ABSTRACT

Catalytic (H_3VO_4) oxidative dehydrogenation (ODH) mechanistic studies of the activation of *n*-hexane have been conducted by means of Density Functional Theory (DFT).

Catalytic oxidative dehydrogenation is an important strategy for the conversion of alkanes to alkenes to provide useful chemical feedstocks from saturated hydrocarbons. Transition metal oxide catalysts based on vanadium provide an important class of catalysts for this reaction. The catalyst is usually prepared with vanadium in a high oxidation state prepared as an over layer supported on a relatively inert main group oxide (silica, alumina, etc.). Activation of the hydrocarbon is then energetically possible through the reduction of vanadium cations which can be subsequently re-oxidised using molecular O_2 to complete the catalytic cycle.

The aim of this study was to use density functional theory to explore the catalytic mechanism of this type of reaction using the conversion of *n*-hexane to 1- and 2-hexene as an illustrative example. Calculations are performed for the 1- and 2-hexene radical pathways and the results extrapolated to discuss the expected selectivity under laboratory experimental conditions (573, 673 and 773 K). Consideration of 3-hexene is excluded as in our earlier experimental studies and in the general literature this product is not reported. The stationary points on the potential energy surfaces were characterized and the associated geometries and relative energies ($\Delta E^{\#}$, ΔE, $\Delta G^{\#}$ and ΔG) were determined. The relative energies of all intermediates and transition states identified are used to lend insight on the mechanistic pathways for the reaction.

We have concentrated on the role of the transition metal in this chemistry and so the catalyst model chosen is an isolated, tetrahedral H_3VO_4 cluster containing one vanadyl bond, V(V)═O. The calculated rate-limiting step is the C─H bond activation (*β*-hydrogen abstraction) from the C_6H_{14} chain by the vanadyl O, with a calculated $\Delta E^{\#} = +27.4$ kcal/mol. This produces a $C_6H_{13}HOH_3VO_3$ complex as an intermediate with vanadium reduced to V(IV). There are then two possible routes for the propagation step that leads to 2-hexene. Firstly, the abstraction of the second γ-hydrogen on the radical intermediate fragment ($\cdot C_6H_{13}$) can take place on a different active V(V) = O site. Secondly this step may involve reaction with gas-phase molecular O_2. These alternatives are compared computationally and results used to discuss some existing experimental data.

1. Introduction

Transition metal oxides are frequently used as heterogeneous catalysts for oxidation of hydrocarbons to produce a variety of products. Gas phase studies of metal oxide clusters and their reaction behaviour can help to understand the mechanism of elementary reactions in catalytic processes under isolated, controlled, and reproducible conditions [1–3].

Vanadium oxide-based catalytic systems are known to be active and selective in many oxidative dehydrogenation (ODH) reactions [4–8]. Studies [9] (Zhanpeisov), [10] (Bronkema, Leo, & Bell) have shown that depending on the method of preparation, vanadium oxide-based catalysts possess phases that include isolated VO_4 tetrahedral sites, comprising one vanadyl bond (V = O), and other phases made up of the dimeric V─O─V species. The V = O bond has been proposed by many investigators to contain a critical oxygen involved in hydrocarbon oxidation reactions [11–15]. Pieck et al. [16] (Pieck, Banares, & Fierro) studied the ODH of propane on V_2O_5/ZrO_2 catalysts and showed that monovanadates have both higher activities and better selectivities to propene than bulk V_2O_5 and polyvanadates. However, generally at high conversions of the alkane, non-selective combustion pathways limit the alkene selectivities, regardless of the good activity for the ODH of

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alkanes to their corresponding alkenes [17–19]. For example, it is well established that limited propene selectivity at higher propane conversions is related to propene adsorption on acid sites and their subsequent combustion to carbon oxides [20] (F. Arena), [21] (Y.-M. Liu). Much effort has been spent over the last decades to develop suitable vanadium oxide-based catalysts for the oxidative dehydrogenation and selective oxidation of light hydrocarbons to valuable olefins and oxygenates [22] (E.A. Elkhalifa and H.B. Friedrich), [23] (F. Cavani), however, these processes are still far from industrial application. Earlier experimental studies indicate that the selective oxidation of propane on vanadium oxides proceeds via a Mars–van Krevelen [24] (Mars & Van Krevelen) (redox) mechanism that involves the reduction of the metal oxide surface by the alkane with the formation of the alkene and water, followed by reoxidation of the surface through gas-phase oxygen.

Reactions comprising isolated vanadate species with a variety of support materials including silica, titania and zirconia were previously modelled with a variety of computational methods [25–28]. Reported work on Density Functional Theory (DFT) modelling of catalytic systems and shorter chain hydrocarbons is extensive [29–31], albeit that on long chain alkanes over vanadium oxide-based catalysts is limited. Although heterogeneous catalysis is largely an experimental field, computational modelling and simulation, as a complementary and supplementary tool, is a prominent field that is increasingly being recognized as important and essential in the study and development of catalytic systems [32–34]. A good model not only helps experimentalists to rationalize their results, but also assist to make predictions that challenge the capability of available experimental techniques in terms of the spatial, time and energy resolutions, and guides experimentalists to design new experiments [35] (G.A. Somorjai Y. L., Major successes of theory and experiment-combined studies in surface chemistry and heterogeneous catalysis). Our research group has published a number of experimental papers involving ODH of *n*-hexane and higher alkanes over VMgO catalysts [36–39]. The relatively low yields of olefins and aromatics that were obtained in laboratory experiments necessitated this theoretical study. One of the aims of this work was to determine the most active O site, as either the vanadyl O or the bridging O, in *n*-hexane elementary oxidation reactions to hexenes. The merits of the oxidative dehydrogenation (ODH) conversion of inexpensive alkanes to produce value added products, such as olefins and aromatics, represents the driving force that motivates the research for developing active and selective catalysts for this purpose [40] (E.A. Elkhalifa, Oxidative dehydrogenation and aromatization of *n*-octane over VMgO catalysts obtained by using different MgO precursors and different precursor treatments).

Our recent publication on the gas-phase non-catalytic ODH of *n*-hexane show that the rate-determining step is the abstraction of β-hydrogen by molecular O_2 [41] (N.E. Damoyi H. F.). We proposed that molecular O_2 plays an important role in the radical propagation steps through the intermediates, to produce 1- and 2-hexene and the more reactive $\cdot$OH and HO_2 radicals. Since our present studies include both molecular O_2 and isolated H_3VO_4, we therefore seek to compare the contribution of H_3VO_4 and O_2 in the activation of *n*-hexane and radical propagation steps to produce 1- and 2-hexene. Although our modelling is an oversimplification of heterogeneous surface reactions because of the methodology followed, namely, gas-phase calculations on isolated active sites, we believe that the results will be essential in acquiring a theoretical baseline for future potential periodic-DFT calculations of this system. Furthermore, comparisons of the results with those obtained in our recent work [41] (N.E. Damoyi H.F.) on gas-phase non-catalytic ODH of *n*-hexane would be useful, since under certain experimental conditions, gas-phase ODH mechanisms may compete with the catalytic ODH mechanisms. A second study that used a bigger model ($H_4V_2O_7$ as catalyst) is being finalised for publication.

The activation energies ($\Delta E^{\#}$), electronic energy (ΔE) and Gibbs energy (ΔG) changes were calculated and these properties facilitate the elucidation of the likely intermediate species involved and the mechanistic pathways followed for the transformation of *n*-hexane to 1- and 2-hexene.

2. Theoretical methodology

2.1. Computational details

Gas-phase DFT calculations were performed using the Gaussian 09W package [42] (Frisch & et. al.) incorporating the Gausview 5.0 graphics interface. All calculations were performed on a cluster based at the Centre for High Performance Computing (CHPC) in Cape Town, South Africa. All the structures were optimized without constraints and the harmonic vibrational frequencies performed using the B3LYP hybrid functional, which combines Becke's three-parameter nonlocal hybrid exchange potential and the nonlocal correlation functional of Lee, Yang and Parr [43] (Becke), [44] (Lee, Yang, & Parr). This functional is known to provide a good description of the potential energy surface (PES) of transition metal-containing compounds [45–47]. The 6–311 + g(d,p) basis set was employed for C, O and H atoms and the V atom described using the relativistic Stuttgart effective core potentials (ECPs) [48] (Dolg, Wedig, Stoll, & Preuss), [49](Martin & Sundermann). The transition states (TS) were determined by using relaxed-PES scan techniques on the closed shell and open-shell singlet systems and the laboratory experimental conditions, namely 573, 673 and 773 K, were utilized. The intrinsic reaction coordinate (IRC) calculations in the mass-weighted internal coordinate system, using the algorithm developed by González and Schlegel [50] (Gonzales & Schlegel), [51] (Gonzales & Schlegel), were conducted to confirm the connection of transition states to related minima. The natural bonding orbital (NBO) calculations were performed using the NBO 3.1 program as implemented in the Gaussian 09W package and the donor–acceptor interactions were analysed based on second order perturbation theory analysis of Fock matrix in NBO basis [52] (Carpenter & Weinhold), [53] (Carpenter & Weinhold, The structure of small molecules and ions).

2.2. Model system

Fig. 1 displays the structure of the selected model of the proposed active site, namely the H_3VO_4 monomeric unit with vanadium in a tetrahedral coordination sphere. This model has been utilized before in DFT modelling studies of similar systems [54](L. Gracia P. G.-N.), [55] (Lei Cheng G. A.). The structure has one V═O bond with vanadium in its highest oxidation state (+5), and the three H atoms are added to balance the −3 charge on the three O atoms. In all calculations the atoms were allowed to relax. Comparisons of some calculated parameters and vibrational spectra of the model structure with experimental values show that the percentage errors in the calculated V═O bond length is 1% and that of the V─O bond length is 3%. The calculated percentage error for the V═O stretching vibration is 6%. Cartesian coordinates of optimized structures are included with supplementary material.

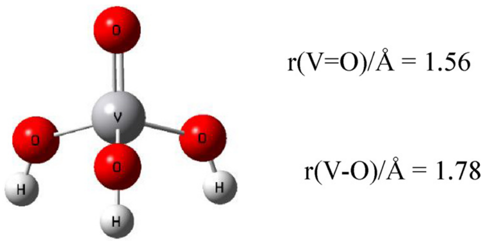

Fig. 1. H_3VO_4 model. B3LYP/6-311 + G(d,p) for H and O atoms, and Stuttgart ECPs for the V atom.