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A DFT study of the ODH of n-hexane over isolated H₃VO₄ and H₄V₂O₇

Catalytic (H₃VO₄ and H₄V₂O₇) oxidative dehydrogenation (ODH) mechanistic studies of the reaction of n-hexane to 1- and 2-hexene have been conducted by means of Density Functional Theory (DFT).

The aim of this study was to gain insight about the catalytic mechanistic pathways for the conversion of n-hexane to 1- and 2-hexene. The 3-hexene pathway was omitted because the isomer is not observed in our experiments, nor reported in literature. The chosen models for the study were the isolated H₃VO₄ and H₄V₂O₇ clusters, with the H₃VO₄ unit comprising one vanadyl bond, V(V)=O, and the H₄V₂O₇ cluster comprising two vanadyl bonds and the bridging O atom in the V(V)-O-V(V) unit. The calculated rate-determining step is β -hydrogen abstraction from the C₆H₁₄ chain by vanadyl O to produce the complex intermediates with reduced V(IV) centres in accumulated V(IV)-OH bonds and activation barriers of $\Delta E^\ddagger = +27.4$ (H₃VO₄) and $+32.7$ (H₄V₂O₇) kcal/mol. Both these values are lower than the value calculated for the H-abstraction by the bridging O in H₄V₂O₇ ($\Delta E^\ddagger = +43.9$ kcal/mol). The energetically favourable propagation steps that may lead to olefins involve α -H abstraction (1-hexene) and γ -hydrogen abstraction (2-hexene) on the radical intermediate fragment (\cdot -C₆H₁₃) by vanadyl O from a different site or by gas-phase molecular O₂. The gas-phase pathway may dominate at lower n-hexane to oxygen molar ratios combined with low V(V)=O surface areas and be subdued at higher molar ratios in combination with high V(V)=O surface areas. However, chemisorption of the radical intermediate (\cdot -C₆H₁₃) on the surface O sites may lead to undesired products including oxygenates. This may explain the low yields of 1- and 2-hexene (< 20%) obtained in our laboratory experiments. H-transfer between two V(IV) centres (accumulated V(IV)-OH) reproduces V(V)=O, and also V(III) and H₂O. The reoxidation of reduced V(III) to V(V) occurs through Mars-van Krevelen mechanism.

All structures on the potential energy surfaces (PESs) were optimized using the GAUSSIAN 09W program, at the B3LYP level, with the 6-311+g(d,p) basis set for C, O and H atoms and effective core potentials (ECPs) for the V atom. The laboratory experimental conditions of 573, 673 and 773 K were included in the computations. The most energetically favourable pathways for the reaction were determined from some calculated kinetic and thermodynamic properties (ΔE^\ddagger , ΔE , ΔG^\ddagger and ΔG) and the catalytic mechanism that is likely to be followed will be discussed.

Presenter Biography

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1. Teaching and Learning

I joined the department of Chemistry at Mangosuthu University of Technology (MUT) in 2003. Presently I am senior lecturer and teach Inorganic Chemistry subjects within the department and am presently enrolled for the Post Graduate Diploma in Higher Education (PGDHE) at Rhodes University. I received a Vice Chancellor's Teaching and Learning Silver Award in the category of Established Teacher in 2017. In the same year I graduated with a PhD degree in Chemistry at UKZN under the supervision of Prof. H. Friedrich and Prof. G. Kruger. My PhD thesis title was "DENSITY FUNCTIONAL THEORY STUDIES OF THE NON-CATALYTIC AND CATALYTIC OXIDATIVE DEHYDROGENATION REACTION OF n-HEXANE TO 1- AND 2-HEXENE".

1. Research Projects 2.1 Project Title: DFT modelling studies of the reaction of n-hexane to benzene. The research involves utilizing Density Functional Theory (DFT) methods to model the non-catalytic (gas phase) and catalytic (VMgO-type catalysts) oxidative dehydrogenation (ODH) and cyclization reaction

of n-hexane to benzene under laboratory experimental conditions (1 atm. and 573 to 773 K). The intermediates involved, including olefins and aromatics are valuable starting materials for many organic compounds. Computational chemistry through some kinetic and thermodynamic properties is used to provide insight to reaction mechanisms. This work is presently being conducted in partnership with the Catalysis Research Group (CRG) under Prof H. Friedrich (UKZN-Westville), Prof H.G. Kruger (UKZN-Westville) and Prof. D. Willock (Cardiff University, UK). Calculations are run through the Centre for High Performance Computing (CHPC) in Cape Town, South Africa. The Gaussian 09W code is utilized together with the GaussView 5.0 graphics interface. This work has produced two publications and more publications are pending.

2.2 Project Title: Ab initio studies of the 1,3-cycloaddition reactions of 1,3-dipoles (nitrous oxide, hydrazoic acid and diazomethane) with some dipolarophiles.

This project relates to gas and liquid phase modelling of some 1,3-cycloaddition reactions by ab initio computational methods. Some of the involved intermediates and products are important in pharmaceutical and other industries. This project is run in partnership with emeritus Prof T.

Ford (UKZN-Westville) and Prof H.G. Kruger (UKZN-Westville).

Calculations are run through the Centre for High Performance Computing (CHPC) in Cape Town, South Africa. The Gaussian 09W code is utilized together with the GaussView 5.0 graphics interface. A number of publications are pending.

2.3 Prospective Projects

Generally, DFT and ab initio methods in order to understand catalytic and non-catalytic reaction mechanisms of both organic and inorganic reactions.

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