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

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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 ΔE# = +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 (ΔE# = +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 (·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 (·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 773K were included in the computations. The most energetically favourable pathways for the reaction were determined from some calculated kinetic and thermodynamic properties (ΔE#, ΔE, ΔG# and ΔG) and the catalytic mechanism that is likely to be followed will be discussed.

HPC content

Code: GAUSSIAN 09W program
Memory: Default (memory not specified in input)
Node: 1
Walltime: 96:00
File Transfer To Desktop Windows Computer: SSH Secure Shell Client

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