

Quantum Mechanical Calculations of O(³P) Reactions with Cyclohexene Chemisorbed onto Al₂O₃

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Petroleum processing generates an important fraction of relatively inert hydrocarbon compounds with little commercial value. The ever-increasing worldwide demand of petroleum and its derivatives, along with the depletion of light crude oil supplies, has increased the proportion of these hydrocarbon residuals generated in refineries. Thus, the need of new greener technologies to functionalize these organic compounds is paramount. Yet, technologies that oxidize and functionalize hydrocarbons, such as non-thermal plasma processing, have been largely overlooked because hydrocarbons can partition the gas phase, making the reaction with plasma difficult to control. Here, we present an alternative pathway that prevents the hydrocarbon partition to the gas phase by adsorbing it onto an active metal oxide surface. Upon adsorption, the properties of the organic molecule change, leading to different reaction pathways to be energetically possible.

In this work, the chemisorption of cyclohexene on alumina was modeled and correlated to experimental data. The energy minimization and vibrational frequency calculations were performed on a binuclear cluster including an Al₂O₃ active site. These calculations revealed where a chemisorbed cyclohexene had a lower electron deficiency than a free gaseous cyclohexene, indicating the position of the chemisorption bond between it and alumina. In addition, the energies of several reactions of cyclohexene and radical oxygen on the surface were calculated. The experimental data indicates multiple oxidations of cyclohexane, leading to the ring being opened and ultimately the formation of carbon dioxide.