Weerayuth Panyaburapa 2006: The Partial Oxidation of Unsaturated Hydrocarbons with H_2O_2 over TS-1 Investigated by ONIOM Method: Formation of Active Site and Reaction Mechanism. Master of Science (Chemistry), Major Field: Physical Chemistry, Department of Chemistry. Thesis Advisor: Professor Jumras Limtrakul, Ph.D. 75 pages.
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The mechanism of alkene oxidation with hydrogen peroxide over the defect titanium silicalite-1 (TS-1) was investigated at the density functional theory using the 9T B3LYP/6-31G(d,p) cluster and the two-layered 9T/65T ONIOM(B3LYP/6-31G(d,p):UFF) cluster scheme. The titanium hydroperoxo intermediate in bi-dentate manner, Ti(η^2-OOH), occurring through the single-step double proton transfer mechanism with the assistance of a neighboring silanol group, was proposed to be an active species in the oxidation process. This species was found to be susceptible to the number of water molecules surrounding the active region. The introduction of an additional water molecule into the hydrated Ti(η^2-OOH) complex results in the formation of titanium peroxo species, Ti(η^2-OO$^-$), in accordance with the role of water in hydroperoxo-peroxo interconversion in the TS-1/H_2O/H_2O_2 system. The oxygen abstraction step in the epoxide formation was found to be the reaction rate determining step, and was sensitive to a number of methyl groups substituted to the active C=C bond of alkene molecules. The 30T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) apparent activation energies for ethylene, propylene, and *trans*-2-butylene were estimated to be 15.5, 13.6, and 12.2 kcal/mol; respectively, in agreement with the reactivity series of the gas phase calculations and comparable with available experimental apparent activation energy of 1-hexene of 15.5±1.5 kcal/mol.

Student's signature

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