Sarawoot Impeng 2010: Structures and Reactivity of Propane over Nanostructured Zeolites: A Newly Developed DFT Approach. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Mr. Somkiat Nokbin, Ph.D. 106 pages.

The hydrogen exchange reactions of propane adsorbed over H-FAU zeolite were studied by the ONIOM(B3LYP/6-31G(d,p):UFF) approach. The H/H exchange reactions occur via both primary- and secondary hydrogen exchange mechanisms at the primary- and secondary carbon atoms of the propane molecule, respectively. These two exchange processes proceed via the carbonium ion-like transition state which is in agreement with the experiment study in literature. The corresponding apparent activation energies are calculated to be 27.3 and 26.5 kcal/mol for primary- and secondary hydrogen exchange reactions, respectively, which are close to the previous available experimental study of H/H exchange reaction over H-ZSM-5 zeolite. Our results suggested that the primary- and secondary hydrogen exchange of propane over acidic zeolite are competitive reactions.

Propane cracking over different types of zeolites was investigated using the realistic nanocluster of 120T performed at the M06-L/6-31G(d,p)//ONIOM(M06-L/6-31G(d,p):UFF) level of theory. The adsorption energies of propane for cracking reaction are predicted to be -7.6 and -9.9 kcal/mol for H-FAU and H-MOR, respectively. Using the experimental adsorption energies as the benchmark, our combined ONIOM scheme is found to represent the interaction of propane with zeolites. After adsorption, the zeolite's proton inserts into a C-C bond of a propane molecule, yielding a methane and ethoxide intermediate. Subsequently, the methane molecule is desorbed before the deprotonation of the ethoxide intermediate, resulting in the formation of the ethylene product. The protonation step is found to be rate-determining with the actual activation energies of 43.7 and 41.3 kcal/mol for H-FAU and H-MOR, respectively. The activation energies for the deprotonation step are 24.7 and 18.5 kcal/mol for H-FAU and H-MOR, respectively. Our findings suggest that the propane cracking was insensitive to the zeolite structure.

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