Bundet Boekfa 2009: Structure, Reaction Mechanism and Dynamics of Hydrocarbons over Zeolites: Electronic Structure Theory Approaches. Doctor of Philosophy (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Professor Jumras Limtrakul, Ph.D. 99 pages.

The confinement effect of zeolite on the adsorption and reaction was studied with hybrid methodologies: ONIOM and embedded ONIOM (the ONIOM model embedded in the electrostatic potential field of periodic lattice). The interactions of saturated and unsaturated hydrocarbons over industrially important zeolites (H-MOR and H-FAU) were studied. The calculated adsorption energies of ethane, propane and n-butane in H-FAU and H-MOR with the ONIOM method are in good agreement with the experimental data. For the adsorption of alkenes in acidic zeolite, the adsorption energies for ethene, propene and 1-butene were predicted to be -9.4, -11.3 and -12.5 kcal/mol in H-FAU and -10.1, -13.8 and -17.4 kcal/mol for ethene, propene and 1-butene in H-MOR, respectively. These energies are in the range of the experimental data. For the polar molecule, acetone in H-FER, H-ZSM-5 and H-MCM-22 were calculated; the adsorption energies are -25.9, -26.3 and -25.1 kcal/mol for H-FER, H-ZSM-5 and H-MCM-22, respectively. The calculated adsorption energies of acetone compare well with the experimental data. For interaction with amino acid molecules, the adsorption of glycine and L-alanine on H-ZSM-5 were studied. The most stable adsorption structure involves the ion-pair interactions between the protonated amino acid molecule and the anionic zeolite with the computed adsorption energies of -31.3 and -34.8 kcal/mol for glycine and L-alanine, respectively. The other two adsorption complexes via hydrogen bond interaction through the carboxylic and the hydroxyl group of the amino acids are also found and have lower adsorption energies. The zwitterion form of glycine was found to be stable over Na-ZSM-5 with the adsorption energy of -24.8 kcal/mol. The framework effect on the reaction properties was studied via the tautomerization of acetone on H-FER, H-ZSM-5 and H-MCM-22. The activation energies are 30.0, 23.0 and 16.6 kcal/mol for H-FER, H-ZSM-5 and H-MCM-22, respectively. H-MCM-22 is found to be the most efficient catalyst for the reaction due to it having the smallest constrains influence on the transition structure. The confinement effect of the zeolite framework on the adsorption and reaction properties of hydrocarbon can be correctly described with the ONIOM model and lead to the differentiation of the adsorption and hydrocarbon activation process with different types of zeolites.

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