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Two hybrid computational schemes and molecular dynamics simulations were used to study structure, adsorption, reaction and diffusion mechanisms of adsorbed molecules in industrial nanomaterials. The embedded cluster model derived by SCREEP method was proven successful to predict the potential energy surface of the ethylene protonation reaction in H-FAU zeolite. The inclusion of the electrostatic potential of the infinite crystal enhanced the binding energy and the degree of proton transfer to the ethylene by lowering the activation energy. The calculated adsorption energies and activation energies are in good agreement with the experimental reports. This method was not only successful in predicting the energy pathway, but also in differentiating the reactivity of different types of zeolites. To model the confinement effects on the adsorption process of the adsorbed molecules of a size comparable to the zeolite pores, the ONIOM method based on the extrapolation principle was applied. The combination between different levels of calculation (the electron correlation methods and the universal force field (UFF)) was carefully calibrated and used to predict the adsorption energies of *o*-, *m*-, and *p*-xylene in H-ZSM-5 zeolite. The range of adsorption energies of 18-22 kcal/mol was in close agreement with the heat of adsorption inferred from experimental data.

Molecular dynamics simulation studies of *p*-xylene in silicalite revealed that the diffusion mechanism resembles the process of jump diffusion in which the *p*-xylene molecules preferentially spend rather long periods of time at the channel intersection sites before changing rapidly to the other sites. The detailed microscopic pictures supported the experimental observation that, at loadings higher than 4 molecules per unit cell, the intersections and sinusoidal channels are filled up simultaneously, while there is no occupancy in the straight channels. In order to study the diffusion of *p*-xylene in the mesoporous MCM-41, the intermolecular force field was newly developed for this system. The simulated adsorption energies obtained by using the novel force field were primarily associated with the van der Waals interactions of the model whereas the contribution from electrostatic interactions is relatively small (about 2 kcal/mol). At all loadings considered, *p*-xylene molecules adopted orientation parallel to the wall in the first layer.



Student's signature



Thesis Advisor's signature

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