

Molecular dynamics study of butene cracking intermediates in H-ZSM-5

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Catalytic cracking of C_{4+} alkenes over acidic catalysts, e.g., H-ZSM-5, is employed in various petrochemical processes to upgrade low-value product streams by increasing the light olefin yield. Alkene cracking is generally accepted to occur through a carbenium ion mechanism. Recent studies have indicated that for butene cracking, most of the products are obtained through a dimerization-cracking mechanism, implying that C_8 intermediates are formed prior to cracking.[1] Previous DFT studies on isobutene protonation have shown the importance of taking into account the entropy loss upon alkoxide formation and concluded that at actual cracking temperatures a tertiary ion appears to be more stable than an alkoxide.[2,3] However, it is still an open question whether carbenium ions are long-lived inside the zeolite pores or rapidly evolve, either by binding to the framework, forming an alkoxide, or by deprotonating, forming a π -complex (see Figure 1).

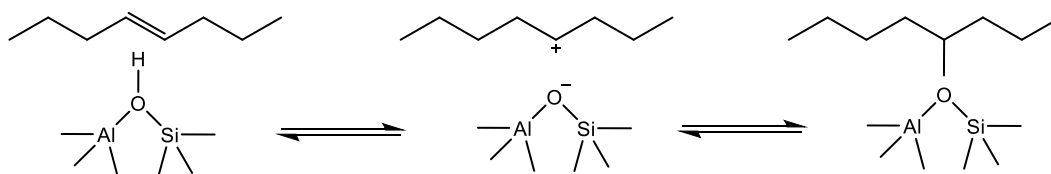


Figure 1. Three possible adsorption states for a linear C_8 chain: a physisorbed π -complex (left), a chemisorbed carbenium ion (center) and alkoxide (right)

In this work, the dynamic behavior of various intermediates in the butene cracking mechanism is investigated using ab initio molecular dynamics simulations at actual cracking temperatures. With this technique, the free energy surface is sampled, taking into account the conformational freedom of the C_8 species and the lattice flexibility. Regular transitions between the physisorbed and chemisorbed states are observed. C_8 carbenium ions appear to be long-lived intermediates inside the zeolite pores, in contrast to C_4 carbenium ions. Rapid isomerizations through hydride shifts allow the positive charge to occupy different positions along the carbon skeleton, although the simulations reveal a preference for central chain positions and tertiary carbon atoms.

[1] Meng, X., Xu, C., Li, L., Gao, J., Energy & Fuels, 24 (2010) 6233

[2] Nguyen, C.M., De Moor, B.A., Marin, G.B., J. Phys. Chem. C, 116 (2012) 18236

[3] Tuma C., Sauer J., Angew. Chem., 117 (2005) 4847