

Probe molecule transformations for staining techniques in zeolites – A periodic DFT study

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The so-called probe molecules for staining techniques facilitate the direct experimental investigation of the acid site distribution and strength by generating UV active species in situ inside the zeolite. We investigated the formation of such fluorescent (oligo)thiophene derivatives in three characteristic sites of acidic ZSM-5 zeolite. The acidic sites were modeled in the straight and sinusoidal channels and in their intersection by substituting one silicon atom to Al at the T5, T10 and T12 sites (Si/Al ratio of 95), respectively, and neutralizing the remaining negative charge with a proton. First, the most plausible acid catalyzed decomposition/oligomerization pathways of thiophene were determined using a cluster model, which were then implemented into the various channels of the zeolite using MFI framework with periodic boundary conditions. We found that the adsorption of thiophene on the acidic site is followed by the protonation at C1 carbon atom in an energetically uphill process. The generated carbocationic species, however, readily reacts with excess neutral thiophene molecules to form bithiophene and terthiophene carbocations. The modeled adsorption and emission peaks of the latter species show very good agreement with the experimentally observed and utilized characteristic bands of the staining experiments [1,2]. The specific weak interactions between the zeolite framework and neutral and carbocationic (oligo)thiophene derivatives were also scrutinized with the recently introduced Non-Covalent Interaction method [3,4].

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