

Abstract:

Mechanisms of three reactions catalyzed by microporous materials were investigated computationally; the reactions investigated include Friedländer and Knoevenagel reactions catalyzed by Cu_3BTC_2 metal organic framework (MOF) and an intramolecular cyclisation of unsaturated alcohols catalyzed by zeolite H-ZSM-5. It was found that the reaction mechanisms of all three reactions are controlled by a high concentration of active sites in materials. Reaction intermediates interact with more than one active site simultaneously. This novel concept of “multiple-site” interactions is described. The concerted effect of two catalytic sites leads to a decrease of activation barriers on reaction paths of Friedländer and Knoevenagel reactions. On the contrary, a simultaneous interaction of reactants with two active sites has a negative effect on reaction rate in case of alcohol cyclization catalyzed by H-ZSM-5; it was found that the interaction with dual sites results in the increase of activation barriers and diffusion limitations. In case of Knoevenagel reaction catalyzed by CuBTC, the adsorption of reaction precursor to the reaction site allows the creation of a dynamic defect in the MOF framework that subsequently catalyses the reaction. Both, the multiple sites effect and the dynamical defect formation effect are novel concepts that offer explanations of some properties of microporous materials.