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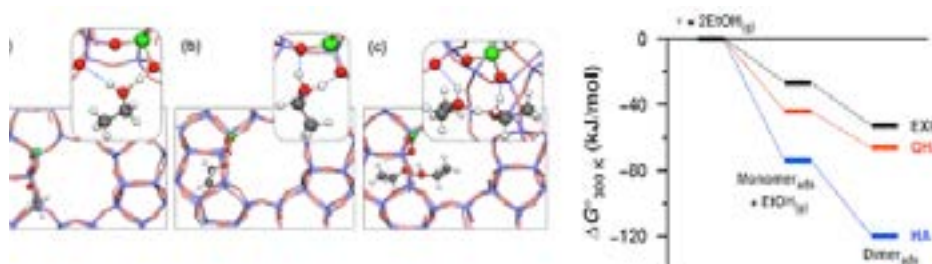
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The role of anharmonicity in the confinement effect in zeolites: Structure, spectroscopy and adsorption free energy of ethanol in H-ZSM-5

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Zeolite is one of promising solid acid catalysts for the conversion of renewable biomass-derived alcohols into fuels and chemicals. Dehydration of alcohols to alkenes is a well-known prototypical acid catalyzed reaction, where confinement and entropic effects impact the rates of these reactions. For such conversions, HZSM-5 zeolite is commonly used as a platform for acid catalyzed reactions due to its strong acidity and enhancement of reaction rates due to confinement in pores. In this talk, we present the structure and thermochemistry of ethanol adsorption on the Brønsted acid site of the HZSM-5 by means of *ab initio* molecular dynamics (AIMD) simulations directly compared with *in situ* IR spectroscopy and thermochemical measurements on the same material. Simulations were performed using two different ethanol loadings (with/without deuterium substitution) at different temperatures ($100 \leq T \leq 700$). This enables us to take into account enthalpic and entropic effects caused by the dynamics of the motion of the reaction intermediates. AIMD simulations show that hydrogen transfer from the zeolite scaffold to ethanol occurs as temperature increases. In the simulations with higher ethanol loading, proton transfer occurs *via* relay between H-bonded ethanol molecules. Calculated projected vibrational density of states (VDOS) obtained from velocity autocorrelation function show a broad peak around 1600 cm^{-1} related to H-O-H bending mode which is also observed experimentally. We estimated entropy and enthalpy of adsorption using the computed VDOS along with a quasi-harmonic approximation, which shows good agreement with experimental measurement conversely, the more commonly employed harmonic vibrations lead to free energy estimates that deviate from experiment substantially. Overall, this study exemplifies how enharmonic effects, as capture by AIMD, are critical for the quantitative modeling of the free energetics of zeolite-catalyzed processes.



Biography

Roger Rousseau is awarded PhD in Inorganic Chemistry from The University of Michigan, USA in the 1995. He holds a Master Degree in Inorganic Chemistry from The University of Michigan, USA in the 1994, followed by a Bachelor's Degree in Chemistry from University of Windsor, Canada in the 1991. Currently, he is working as a Senior Staff Scientist for Pacific Northwest National Laboratory, Richland, Washington. His research interests are focused on the application of quantum mechanical methods in simulations of the properties and reactivity of molecules, solids, and surfaces of relevance to catalysis for energy applications. Currently, He is working on the application and development of *ab initio* molecular dynamics methods to the study of heterogeneous and homogeneous catalysis reaction mechanisms. This includes participation in the Center on Molecular Electrocatalysis, an Energy Frontier Research Center, and PNNL's Institute for Integrated Catalysis.

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