Exploring New Frontiers in Modeling Complex Zeolite-Catalyzed Reactions Using Advanced Molecular Dynamics Techniques

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Introduction

The methanol-to-olefins (MTO) mechanism is a much-discussed topic within heterogeneous catalysis [1]. Currently there is a consensus that a hydrocarbon pool consisting of organic molecules trapped in the zeolite pores acts as co-catalyst. During the last decades, a plethora of theoretical studies was devoted to unravel the reaction mechanism behind this complex process. Hereby, most theoretical procedures still rely on static methods focusing on a limited number of configurations on the potential energy surface [2]. However, such an approach cannot capture all information of the system at realistic operating conditions as its behavior is often too complex. Factors contributing to this complexity encompass framework flexibility, the presence of various guest molecules in the pores, which can take an active role in the chemistry, and entropic factors. Additionally, there may be competing reaction paths connecting two stable energy minima. To capture all these effects, an approach that scans larger portions of the free energy surface is required. In this contribution, the strength and necessity of advanced molecular dynamics techniques for the simulation of complex zeolite-catalyzed chemical transformations is demonstrated by two case studies.

Materials and Methods

Molecular dynamics (MD) simulations of an H-SAPO-34 unit cell containing two acid sites and loaded with different amounts of methanol or water are performed in the isobaric ensemble (NPT) at 350 °C and 1 bar. Metadynamics (MTD) simulations of the benzene methylation reaction by two methanol molecules in a 1x1x2 H-SSZ-24 super cell are performed in the NVT ensemble at 350 °C. All simulations are performed with the CP2K software package, using the revPBE functional and the Gaussian and Plane Wave basis sets (GPW) approach.

Results and Discussion

In a first case study, the behavior of high methanol and water loadings in H-SAPO-34 is investigated. Upon adsorption of methanol or water, the framework significantly expands or contracts respectively. Once a critical amount of methanol or water is adsorbed, we observe a high degree of proton mobility. Excess protons can diffuse through the material by a Grotthuss-like mechanism or a proton vehicle mechanism (Figure 1a), meaning that the actual reactions not necessarily take place at the catalyst's acid site. Moreover, this behavior is known to significantly influence activation barriers of elementary reaction steps [3]. In a second case study, we study the methylation of benzene in H-SSZ-24 by multiple methanol molecules as this is a crucial step in the MTO chemistry for which two mechanisms have been proposed [4].

We show that multidimensional metadynamics simulations are an excellent tool to simulate the competition between the concerted and step-wise methylation mechanism. The transition regions between each of the stable energy minima on the obtained multidimensional free energy surface are relatively broad (Figure 1b), demonstrating that there are no well-defined transition points that describe the investigated reactions due to the large available space in the catalyst pores. Both mechanistic and thermodynamic data can be obtained after a careful analysis of the complex multidimensional free energy surfaces.

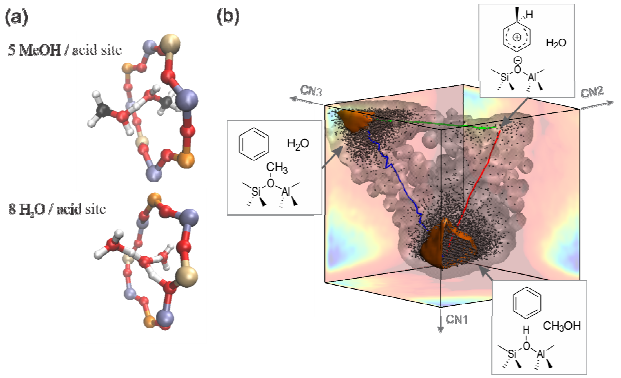

Figure 1.(a) Proton transfer through a H-SAPO-34 8-ring at 350 °C, (b) free energy surface of the benzene methylation with two methanol molecules in H-SSZ-24 at 350 °C.

Significance

We show the potential of advanced molecular dynamics techniques to obtain valuable insights into the complexity of the MTO process. The applied methodology can also be extended to unravel any complex zeolitic process at the nanometer scale level. Dynamical effects like proton mobility can be studied in detail and free energy surfaces of elementary reaction steps at high temperature can be mapped.

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