Ab initio molecular dynamics study on the role of water in the side-chain mechanism during methanol conversion in H-SAPO-34

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Due to the growing relevance of renewable resources, interest in the methanol-to-olefin (MTO) process has grown since it is one of the most prominent technologies to bypass crude oil in light olefin production [1]. This methanol conversion process is catalyzed by zeolite or zeotype catalysts. In particular the chabazite-structured H-SAPO-34 is of industrial interest due to its high light olefin selectivity [2]. Intensive research to elucidate the MTO reaction mechanism led to the general acceptance of the hydrocarbon pool (HP) mechanism [3]. Polymethylbenzenes are identified as dominant HP species in H-SAPO-34 [4], for which the side-chain mechanism is one of the proposed reaction cycles [1].

Due to the development of conversion processes using biomass feedstocks, which contain a high amount of water, the influence of water in the methanol feed on the MTO process is relevant. Experimental research has already shown that the addition of water leads to a reduced coking rate and increased selectivity to light olefins [5]. Although the adsorption behavior of water in H-SAPO-34 has already been investigated by the use of dynamic simulations [6], the water influence on the MTO reaction mechanism is still unclear. Therefore, molecular dynamics and metadynamics simulations are used to investigate the influence of water on the elementary steps of the side-chain mechanism, starting from hexamethylbenzene. The use of dynamic simulations is necessary since static simulations are insufficient to analyze these problems. The results show that water has a significant influence on the stabilization of the aromatic intermediates and on the free energy barriers of the reaction cycle, though a direct interaction is not always clear.

Acknowledgment: We are grateful to the European Research Council.

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