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Adsorption thermodynamics of C1–C4 alcohols in H-FAU, H-MOR, H-ZSM-5, and H-ZSM-22

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ABSTRACT

The adsorption thermodynamics of C1–C4 primary alcohols in large-pore (H-FAU and H-MOR) and medium-pore (H-ZSM-5 and H-ZSM-22) zeolites is quantified using combined periodic DFT-D – statistical thermodynamic calculations. The increase of adsorption equilibrium coefficients with increasing carbon number of the alcohol and with decreasing pore size of the zeolite is attributed to the well-known dispersive van der Waals interactions. Although electrostatic interactions increase in the order: H-FAU < H-ZSM-5 ≈ H-MOR < H-ZSM-22, an interplay with other factors including zeolite acid strength, framework flexibility, and steric constraints globally renders non-dispersive interactions largely similar among the four zeolites. Also, the shape selectivity is probed for adsorption of *n*-butanol, *i*-butanol, 2-butanol, and *t*-butanol at the straight and zigzag channels of H-ZSM-5. A compensation between entropy and enthalpy leads to a difference of at most two orders of magnitude in the adsorption equilibrium coefficient between the two channels.

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1. Introduction

The conversion of alcohols has recently gained much attention from both academia and industry, since it provides a direct chemical route to the “green” production of chemicals and energy [1]. For years, industry has intensively exploited various characteristics of zeolites, such as well-defined microporous structure, acidity and shape selectivity, for a number of alcohol conversion processes, e.g. methanol-to-gasoline (MTG) based on H-ZSM-5 by Mobil Oil [2,3] and methanol-to-olefins (MTO) based on H-SAPO-34 by Norsk Hydro/UOP [4,5], ethanol to ethylene [6] and alcohol to jet fuel [7]. However, a mechanistic understanding of the influence of the zeolite topology and acidity as well as alcohol structure on the conversion kinetics and product selectivity remains rather limited, and the elucidation of the reaction mechanism from experimental data only is extremely difficult [8–24]. One of the main topics of debate is centered on the nature and stability of alcohol–zeolite adsorption complexes that are initially formed over the Brønsted acid sites in alcohol conversion processes [16–24]. As illustrated in Fig. 1, physisorbed (1-HB, 2-HB) and chemisorbed (oxonium) complexes are both stabilized by hydrogen bonding (HB) interactions and differ in the extent to which the zeolite acid proton is transferred to the alcohol [25,26].

In our previous dispersion-corrected periodic density functional theory studies, we have investigated the adsorption energies of the primary C1–C3 and the isomeric C4 alcohols in H-ZSM-5 [25,26]. A variety of possible geometries, including hydrogen-bonded (physisorbed) and protonated (chemisorbed) complexes, were located as stable minima, indicating that the potential energy surface connecting them is broad and very shallow [22,25,26]. The three much debated observed infrared (IR) bands at 2800–2900, 2400–2600, and 1610–1750 cm^{-1} of C1–C4 alcohols adsorbed in zeolites [11–20] were interpreted based on harmonic frequency calculations for the most stable physisorbed and chemisorbed complexes [25,26]. The first region, 2800–2900 cm^{-1}, corresponds to the C–H stretches of both the physisorbed and chemisorbed complexes. The second region, 2400–2600 cm^{-1}, can be assigned to the $H_1–O_1–H_a$ symmetric and asymmetric stretching modes of the chemisorbed complex. The third region, centered around 1600 cm^{-1}, may be attributed to the chemisorbed $H_1–O_1–H_a$ and physisorbed $O_a–H_a$ bending modes [25,26]. It was found that the alcohol proton affinity, as well as dispersive van der Waals (vdW) interactions and steric constraints exerted by the H-ZSM-5 framework, governs the adsorption energies of alcohols. We argued that the reported linearity between chemisorption enthalpy and proton affinity for alcohols [27] and amines [28] is limited to the short-chain bases

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only. Also, the channel preference for the adsorption of C1–C4 alcohols in H-ZSM-5 was predicted based on the calculated electronic energies [23,24]. However, the entropy factor, which plays a significant role in governing the Gibbs free energy stability of the adsorbed complexes in zeolites [29–31] has not been investigated before.

From the solid-state ^{2}H NMR spectra of *t*-butanol and *i*-butanol adsorbed in H-ZSM-5, Stepanov et al. [32–34] deduced that the *t*-butanol molecule is unperturbed when bound to the active site. Since the critical dimension of *t*-butanol (680 pm) significantly exceeds that of the channels (*ca.* 550 pm), this molecule should be accommodated at the channel intersections (*ca.* 900 pm) [30,31]. *i*-Butanol, however, can be located both inside the zeolite channels and at the channel intersections although the latter allow the methyl group to experience a larger rotation rate about the CH_3–CH axis [34].

Mallon et al. [35] determined liquid phase adsorption isotherms for C2–C6 diols and triols in small-pore (H-FER), medium-pore (H-ZSM-5 and H-BEA), and large-pore (H-MOR and H-FAU) zeolites as well as in other ordered mesoporous materials using gravimetry. Henry constants for diol and triol adsorption increase exponentially with carbon number demonstrating that confinement of the adsorbate in the zeolite pores is the driving force for adsorption. This conclusion is supported by the decrease of the propylene glycol adsorption in the Henry regime with increasing adsorbent pore size. Moreover, Oudshoorn et al. [36] studied adsorption of *n*-butanol and *n*-butanol–water mixtures in H-FAU and H-ZSM-5 zeolites. The smaller pore zeolite, H-ZSM-5, exhibits stronger adsorption to gas-phase *n*-butanol. Also, for liquid phase competitive adsorption of *n*-butanol and water, the preference of *n*-butanol over water is more pronounced in H-ZSM-5.

In this work, combined periodic DFT-D – statistical thermodynamic calculations [26,29,37] have been performed to quantify the adsorption thermodynamics of C1–C4 alcohols in large-pore (H-FAU and H-MOR) and medium-pore (H-ZSM-22) zeolites, next to H-ZSM-5 [25,26]. These zeolite frameworks are ideally suited to examine the framework effect since they provide different pore sizes and geometries (Fig. 2). This work provides predictive guidance for the influence of alcohol structure and zeolite characteristics on the adsorption equilibrium coefficients of alcohols in zeolites. Also, accounting for both entropy and enthalpy contributions leads to a more accurate prediction on the channel preference for the adsorption of the butanol isomers in H-ZSM-5.

2. Computational details

2.1. Zeolite models

2-HB physisorption and chemisorption modes [25,26] together with the 1-HB physisorption mode (Fig. 1), in its proper orientation for the further dehydration step [8–10], of C1–C4 primary alcohols have been sampled in H-FAU, H-MOR, H-ZSM-5 [25], and H-ZSM-22. The geometry of all zeolite structures has been taken from the database of the Structure Commission of the International Zeolite Association (IZA) [38,39]. H-FAU is a large-pore zeolite, characterized by supercages with diameter 1300 pm that are interconnected by 12 membered rings (12-MR) with dimensions 740 pm × 740 pm. The acid site is located at the Al_1O_1 position [29,40] and the primitive cell composition is $Si_{47}AlO_{96}H$ (Si/Al = 47). H-MOR is a large-pore zeolite characterized by 12-MR channels (670 pm × 790 pm) in the *c* direction and 8-MR side-pockets (260 pm × 570 pm) in the *b* direction. The unit cell is doubled in the *c* direction and the acid site is located at the Al_4O_2 position [29,41] resulting in a cell composition of $Si_{95}AlO_{192}H$ (Si/Al = 95). H-ZSM-5 is a medium-pore zeolite with intersecting straight (540 pm × 560 pm) and sinusoidal or zigzag (510 pm × 540 pm) 10-MR channels. The acid site is located at the $Al_{12}O_{24}$ intersecting position [25,26,29,41] leading to a unit cell composition of $Si_{95}AlO_{192}H$ (Si/Al = 95). H-ZSM-22 is a medium-pore zeolite with straight channels in the *c* direction with dimensions 460 pm × 570 pm. The small primitive cell is tripled in the *c* direction to ensure sufficient separation of the hydrocarbon images. The acid site is located at the Al_3O_3 position, and the resulting unit cell composition is $Si_{35}AlO_{72}H$ (Si/Al = 35) [29].

All the considered zeolite unit cells have been optimized using periodic DFT-D calculations. The resultant optimized unit cell parameters (Table S1, Supporting Information) have been kept constant in all other subsequent optimizations.

2.2. Periodic DFT-D calculations

2.2.1. Electronic energy calculations

Periodic DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [42] with the projector-augmented wave (PAW) method [43,44]. The total energy was calculated solving the Kohn–Sham equations using the gradient-corrected Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [45]. Brillouin zone sampling was restricted to the Γ point, and convergence criteria on the maximum force and on the electronic self-consistency loop were set at 0.02 eV Å^{-1} and 10^{-6} eV, respectively. The Bader charge analysis [46] was utilized to calculate formal charges of adsorbed alcohol fragments.

In this work, the semi-empirical dispersion-corrected DFT-D approach proposed by Grimme [47] and extended to periodic calculations by Kerber et al. [48] to account for dispersive vdW interactions in the zeolite is used. The total dispersion-corrected energy of a system is thus defined as follows:

$$E_{DFT\text{-}D} = E_{DFT} + E_D \tag{1}$$

where E_{DFT} is the self-consistent Kohn–Sham electronic energy and E_D is an empirical dispersion correction given by:

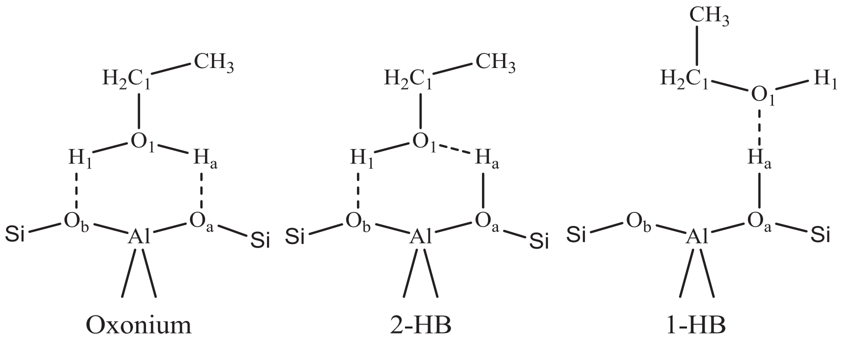

Fig. 1. Oxonium chemisorbed, 2-hydrogen-bonded (2-HB), and 1-hydrogen-bonded (1-HB) physisorbed modes over the Brønsted acid site of zeolite.

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