

Quantitatively predicting the adsorption isotherm of water in H-ZSM-5 using reactive machine learning potentials

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Zeolites have been used for decades as catalysts in the petrochemical industry, with outstanding success. Yet, they are far from retirement. In recent years, zeolites have proven to be highly effective in catalysing innovative, sustainable processes which are expected to be foundational in the chemical industry of the future, for example methanol-to-hydrocarbons (MTH) and biomass conversion [1]. Differently from the traditional oil refinery, these new technologies share a common trait: the ubiquitous presence of water in the catalyst as solvent, reagent, product, intrinsic part of the feedstock or even co-catalyst.

A large effort has therefore been made in recent years to achieve a thorough characterization of water-zeolite interactions [2,3]. From a theoretical perspective, even the simple interaction between a small cluster of water molecules and a pristine, ideal zeolite framework poses remarkable challenges. Indeed, water interacts very strongly with the Brønsted acid sites (BASs) in the material, creating tightly-bound clusters with a mobile hydronium ion (H_3O^+). Additionally, water can directly attack the framework atoms, creating framework-associated and extra-framework aluminium species. This process happens fast and already at room temperature for sufficiently high water loadings [4].

In view of this, it is not surprising that a theoretical characterization of zeolite-water interactions has, up to now, been relegated to (enhanced sampling) molecular dynamics (MD) to explore how a predetermined loading of water behaves in the material [5,6]. While important, the final property that one would be interested in computing is the adsorption isotherm of water in the zeolite – i.e. the amount of water molecule present in the material for different water vapour pressures at a fixed temperature. This is because (1) reactivity in zeolites is highly influenced by the water loading [7,8], which must therefore be known accurately to compute realistic reaction mechanisms and rates, and (2) adsorption isotherms are directly measurable experimentally, providing a tangible link between simulations and the macroscale.

Computing a full adsorption isotherm of water in zeolites has been made impossible up to now by the aforementioned reactive interactions between water and the material, which preclude the usage of standard grand canonical Monte Carlo (GCMC) with classical force fields (FFs). In this contribution, we overcome these issues and report for the first time a complete adsorption isotherm of water in zeolite H-ZSM-5 from reactive transition matrix Monte Carlo (TMMC) simulations of first-principles quality (**Figure 1**). This is made possible by using a highly accurate, reactive machine learning potential (MLP) that can reproduce with outstanding accuracy adsorption energies of water in H-ZSM-5.

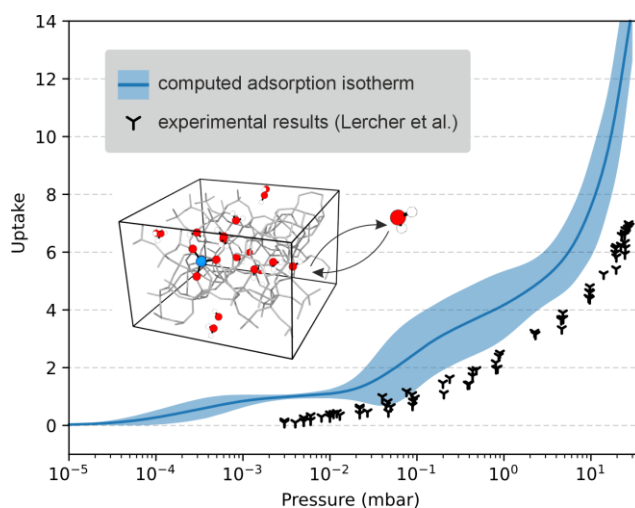


Figure 1

The computed adsorption isotherm of water in H-ZSM-5 derived from MLP-powered TMMC simulations (> 1 ns simulation time, >10⁷ single point evaluations). The experimental data from Lercher et al. [11] is shown for reference.

The MLP is derived from an active learning procedure [9] and is trained on revPBE-D3 reference data, a level of theory that was shown to capture with sufficient accuracy water-zeolite interactions [10]. The adsorption isotherm is derived by first performing long (> 1 ns) MD simulations of all the water loadings of interest (0-20 molecules per unit cell) on multiple active sites locations. We noticed that specific Al locations can form BASs hydrogen-bonded to other framework oxygens, pointing away from the main channel system. This makes such sites particularly sensitive to water and spontaneously form partially hydrolysed $(\text{ZO})_3\text{AlOH}_2$ moieties at room temperature (ZO being oxygen atoms belonging to

the zeolite framework) after nucleophilic attack of water on the Al. These sites are shown to be quite labile and can easily heal if the zeolite is dehydrated at high temperatures.

We selected T1 as model site to compute the full adsorption isotherm of water, reported in **Figure 1**. As it can be seen, the agreement with the experimental data from Lercher et al. [11] is remarkable, where for each considered pressure the difference is of only 1-2 water molecules. This discrepancy is currently under investigation. A logic suspect is the level of theory used to train the MLP (revPBE-D3). Indeed, when compared with recently published chemically-accurate adsorption energies of water in H-ZSM-5 [12], revPBE-D3 was shown to be slightly overbinding, in line with a modest overestimation of the water loading. Simulations are ongoing to further improve this result and confirm the sources of discrepancy with the experiment.

In conclusion, we here propose an unprecedented use of TMMC in combination with MLPs of first-principles accuracy to compute quantitative adsorption isotherms of water in Brønsted-acidic zeolites. The methodology is easily extensible to other zeolite frameworks, for example by building on top of the transferable water-zeolite MLP proposed by Erlebach et al. [13].

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