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MTO MEETS MLIPS:

APPLICATION OF MACHINE LEARNING POTENTIALS TO DIFFUSION OF LIGHT HYDROCARBONS IN SAPO-34

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INTRODUCTION

Methanol-to-olefin process (MTO) in zeolite framework is a multiscale process where product distribution and catalyst deactivation are highly dependent on transport phenomena, e.g., diffusion within the nanoporous structure. Fully ab-initio simulations of these processes are computationally demanding because diffusion takes place on much longer timescales than chemical reactions. Classical force field methods, on the other hand, may not be accurate enough for complex chemical environments encountered within zeolite cages in realistic MTO reaction conditions. [1, 2] In this work we address this problem by using machine learning interatomic potentials (MLIPs) to calculate diffusion barriers for selected molecules in HSAPO-34. This poster presents preliminary results for ethylene diffusion within SAPO-34 with 0, 1, and 2 Brønsted acid sites (BAS), with focus on the targeted MACE model we have trained on DFT data.

METHODS

To calculate diffusion free-energy profiles through 8-member rings of HSAPO-34, we use MLIPs for umbrella sampling in conjunction with WHAM analysis. DFT calculations are used for energy and force evaluations needed for ML training data. General workflow for training of our targeted MACE model is illustrated in Figure 2. Structure of the periodic SAPO-34-unit cell used in these calculations is shown in Figure 1. This model is based on CHA topology from IZA database [3].

DFT

- CP2K
- MOLOPT-DZVP basis set
- PBE + D3
- Planewave cutoff 1000 Ry

MLIP

Pre-trained foundation models

- MatterSim [4]
- Gracemaker [5]

Trained model

- ScaleShiftMACE (Psiflow) [6]

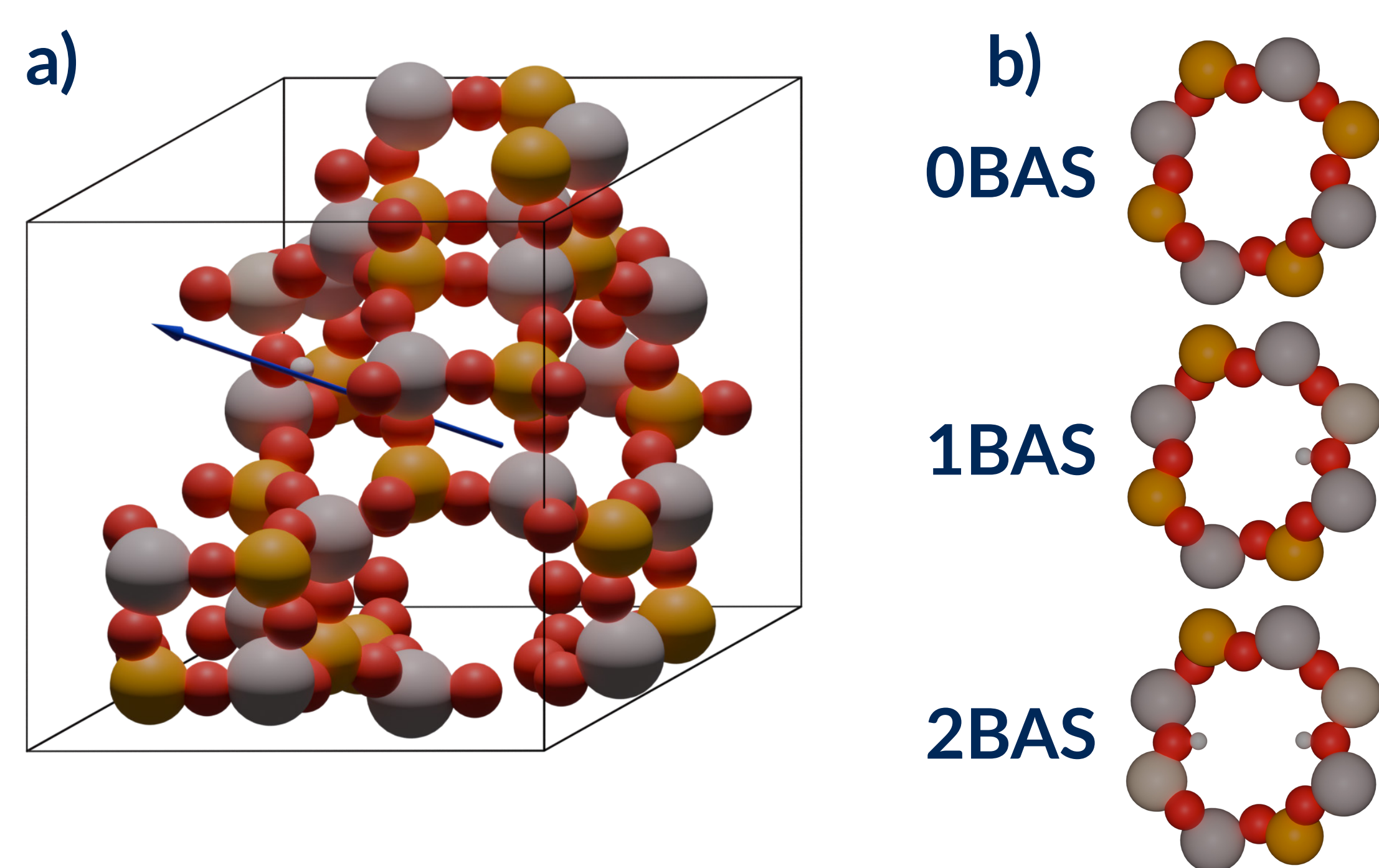


Figure 1. a) Unit cell of HSAPO-34 (1BAS) with diffusion coordinate z visualized as a blue arrow. b) 8-member rings for 0BAS, 1BAS and 2BAS systems.

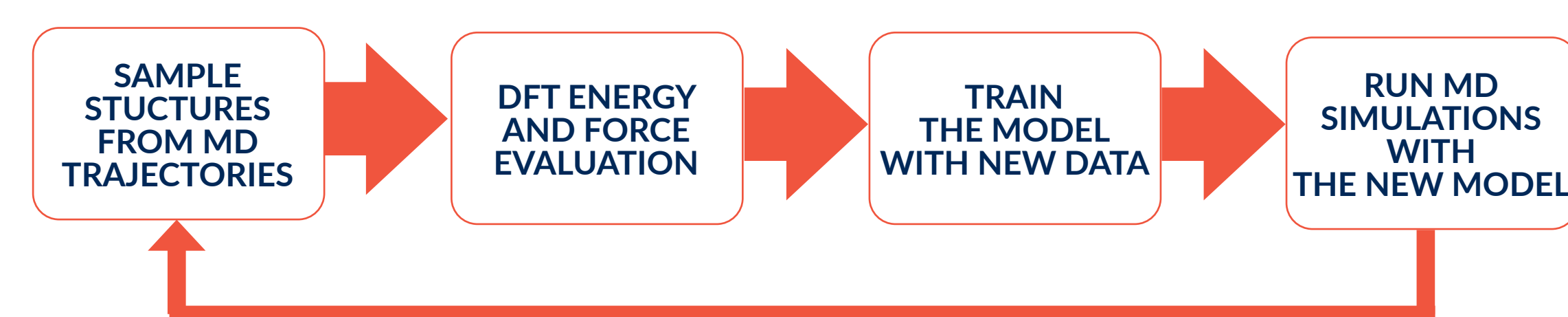


Figure 2. Simplified workflow of the training process.

TRAINING DATA

Our initial automatically sampled dataset consists of over 28000 structures for ethylene and propylene in 0BA, 1BAS and 2BAS HSAPO-34. The current dataset is geared towards ethylene, but future training data will include larger variety of hydrocarbons. Composition of the initial data set can be seen in Figure 3.

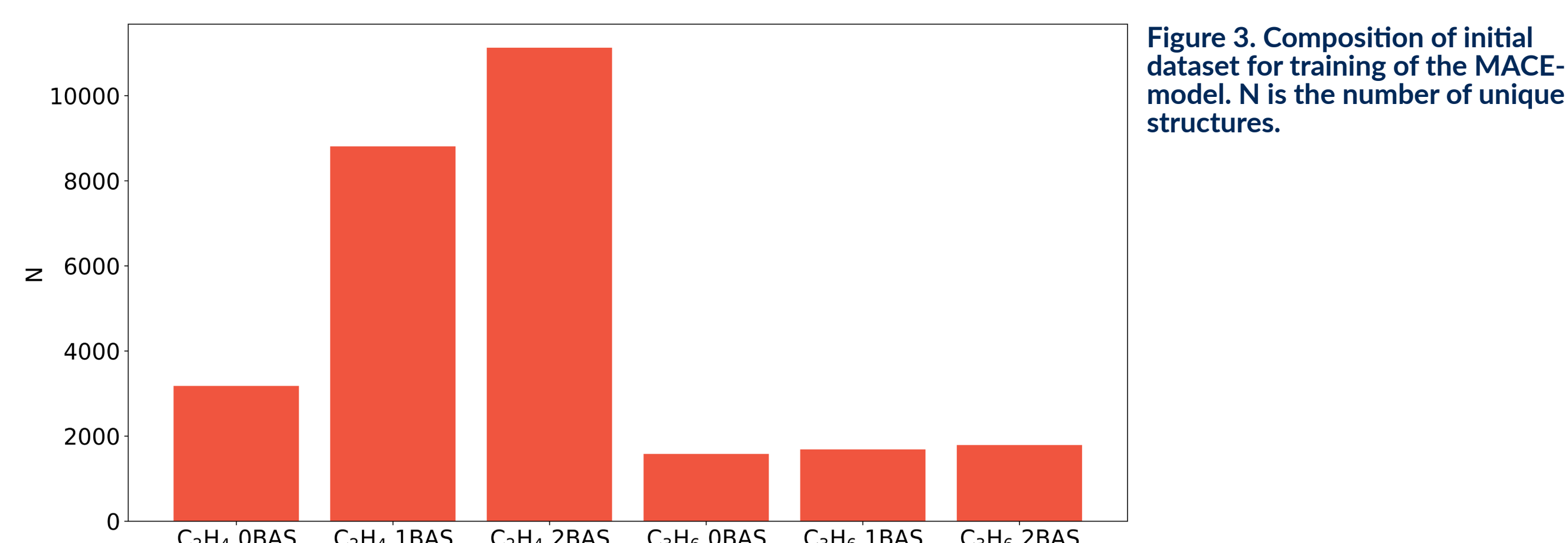


Figure 3. Composition of initial dataset for training of the MACE model. N is the number of unique structures.

ETHYLENE DIFFUSION

Ethylene was deemed as an appropriate test system, as there exists plenty of previous studies on C₂H₄ diffusion in HSAPO-34, including first-principles calculations for diffusion barriers with varying number of acid sites. From previous studies, reported DFT diffusion barriers for 0BAS, 1BAS and 2BAS systems at 600 K are 38 kJ/mol, 20 kJ/mol and 10 kJ/mol respectively. Our targeted MACE-model predicted barriers of 46 kJ/mol, 40 kJ/mol and 27 kJ/mol, effectively showing the promotional effect of acid sites as expected (Figure 4). The best performing pre-trained foundation model, GRACE-2L-SMAX-OMAT-large, gives more accurate barrier for 0BAS system, but fails completely when acid site is added, as can be seen in Figure 5. This failure highlights the need for targeted models for zeolite systems.

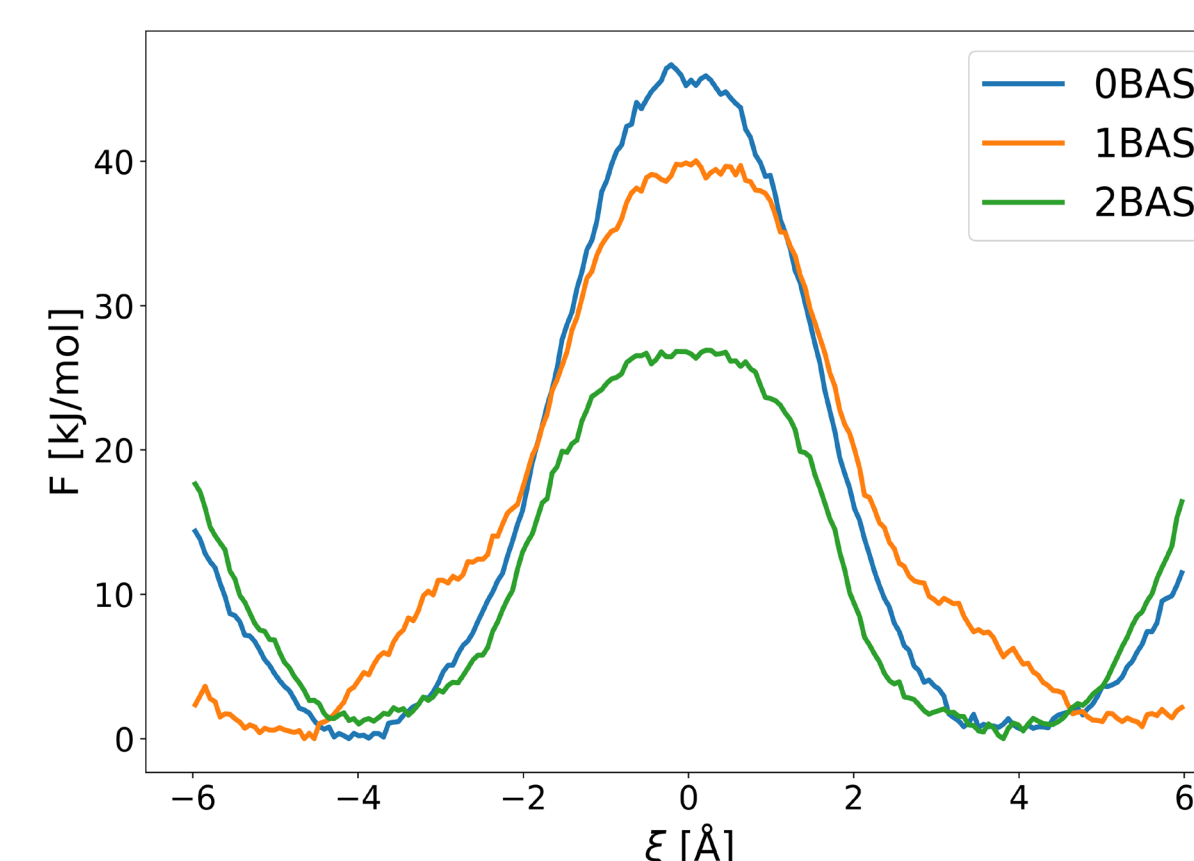


Figure 4. Free-energy profiles for ethylene diffusion in 0BAS, 1BAS and 2BAS systems.

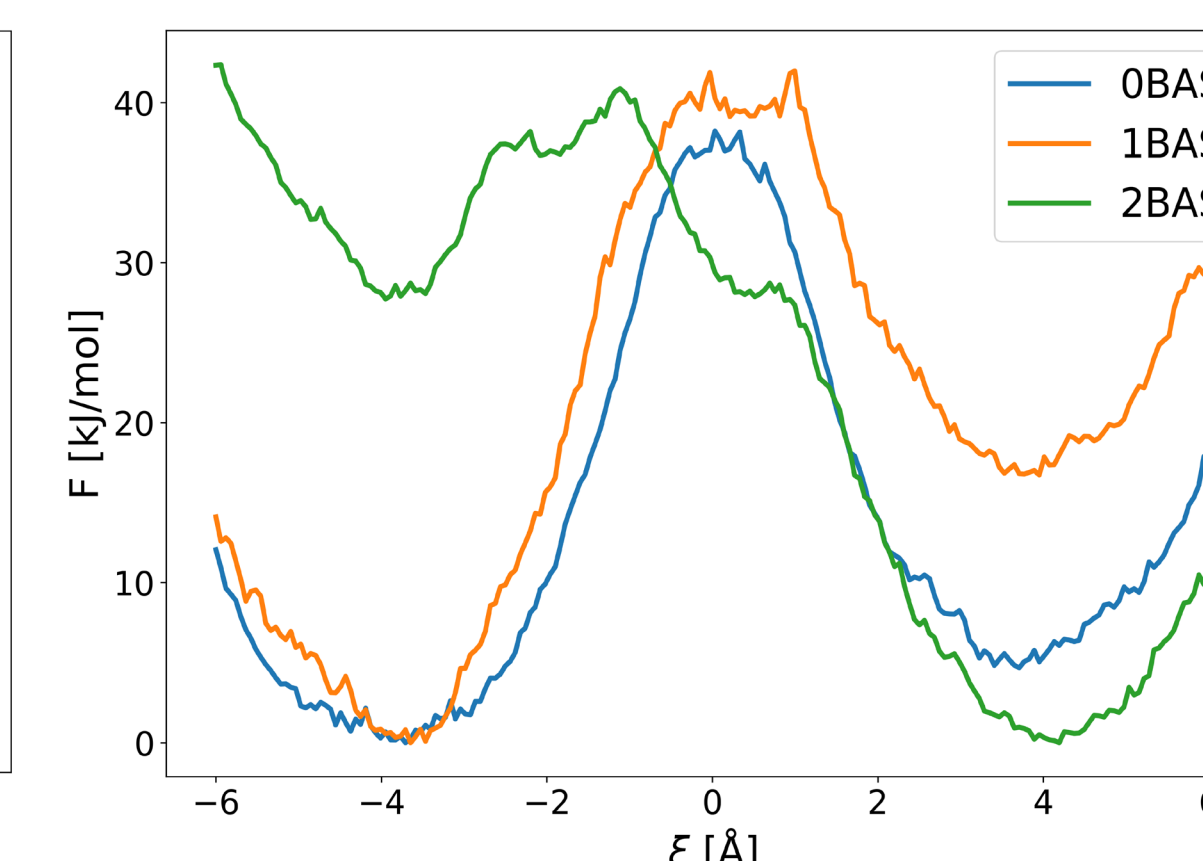


Figure 5. GRACE-2L-SMAX-OMAT LARGE free-energy profiles for ethylene diffusion in 0BAS, 1BAS and 2BAS systems. Model fails to describe 1BAS and 2BAS systems.

CONCLUSION AND FUTURE DEVELOPMENTS

Preliminary results for ethylene diffusion in HSAPO-34 show that targeted machine-learning models trained on DFT data can successfully reproduce trends from DFT diffusion calculations. Building on this, our plan is to extend these MLIP-based methods to higher alkanes and alkenes, as well as metal-exchanged zeolite systems, to gain deeper insights into selectivity and catalyst deactivation in the MTO process.

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