Effect of intracrystalline silanol defects on the diffusivity of benzene in silicalite zeolite

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Introduction

Zeolites are a family of microporous solids which are commonly utilized in industrial applications such as ion-exchange, heterogeneous catalysis, gas adsorption and separation due to their diverse structural characteristics, such as various pore sizes and shapes, chemical compositions and topologies. The structure of zeolites consists of corner sharing $TO_{4/2}$ tetrahedra as the main building unit, in which T is commonly either Si or Al.

Organic structure directing agents (OSDAs) are usually employed to promote the formation of a specific zeolite phase, generating 'defective' structures that differ from the ideal. Upon calcination of the OSDAs, the number of defects is reduced considerably. The presence of silanol defects may alter the structural and chemical properties of zeolites, having a crucial role in their catalytical performance. However, their influence on the diffusive properties of zeolites is yet to be fully unveiled. The diffusion of aromatics has been extensively explored experimentally, but no computational studies have been carried out measuring the effect of these silanol defects on self-diffusivity.

This work focuses on the role of these defects on diffusion. Benzene is an interesting molecule because its self-diffusivity is particularly affected by its tight fit in the 10-ring (straight and sinusoidal) channels of silicalite. Experimental data allows testing the accuracy of the calculation of self-diffusivity by means of molecular dynamics. A recently parameterized general force field allows modeling zeolites of a wide chemical composition with surface defects, including silanols [1]. The simulations at three different benzene loadings and three different temperatures allow to study the role of benzene-benzene interactions in the self-diffusivity, adsorption energy and activation energy of the process. The following results demonstrate the surprising result that benzene self-diffusivity in silicalite is notably increased by the presence of silanol defects.

Objectives

General

- Comparison of the self-diffusivity of benzene in ZSM-5 zeolite with and without silanol defects.
- Determination of adsorption heat of benzene on ZSM-5 with and without silanol defects.
- Reaction coordinate and thermodynamics of defect healing.

Specific

1. Periodic model generation of ZSM-5 zeolite with and without silanol defects.
2. Heat of adsorption and self-difussivity determination by means of molecular dynamics methods.
3. Cluster model generation to describe reaction of defect healing. Transition state search of the defect healing reaction using quantum-chemistry methods.

Materials and Methods

The structure of pure silica ZSM-5 and the corresponding silanol groups were taken from experimental data, and are shown on Figure 1. For the reaction coordinate, a cluster model was generated (Figure 1b). This model changed the siloxy group to a silanol since the protonation happens during the calcination, followed by a condensation reaction between two neighboring silanols. The reaction was modeled by means of Gaussian 16 software, using quantum chemistry semiempirical PM7 method [2]. Benzene diffusion inside ZSM-5 structures was carried out by MD simulations, using DL_POLY Classic 2.20 software with a general zeolite force field [1].
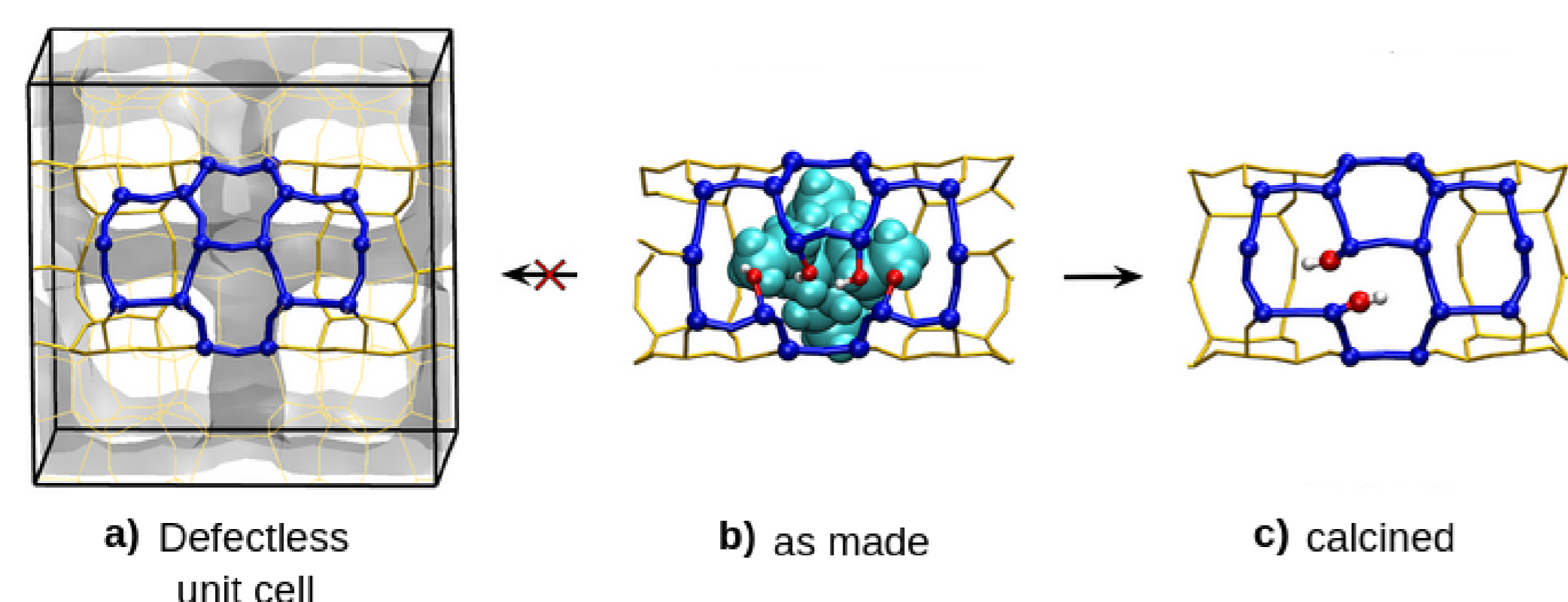

Figure 1: (**a** and **c**) Models of silicalite considered. Starting from the (**b**) as-made material containing four clusters of defects - one of them shown in the image -, one per each OSDA (in cyan) molecule, calcination may produce either a (**a**) defectless zeolite or a (**c**) zeolite with defects. Calcination leads to a structure with 4 silanols per unit cell, which are located in four edge-sharing 6-rings (colored in blue).

Results

Heat of adsorption

The heats of adsorption values are essential in order to check the accuracy of the force field methodology used, since its comparison to experimental results is far more reliable than with diffusivity values. A wealth of accurate calculated and experimental values of heat of benzene adsorption in silicalite are available in the literature, and a balanced summary is shown in Figure 2.
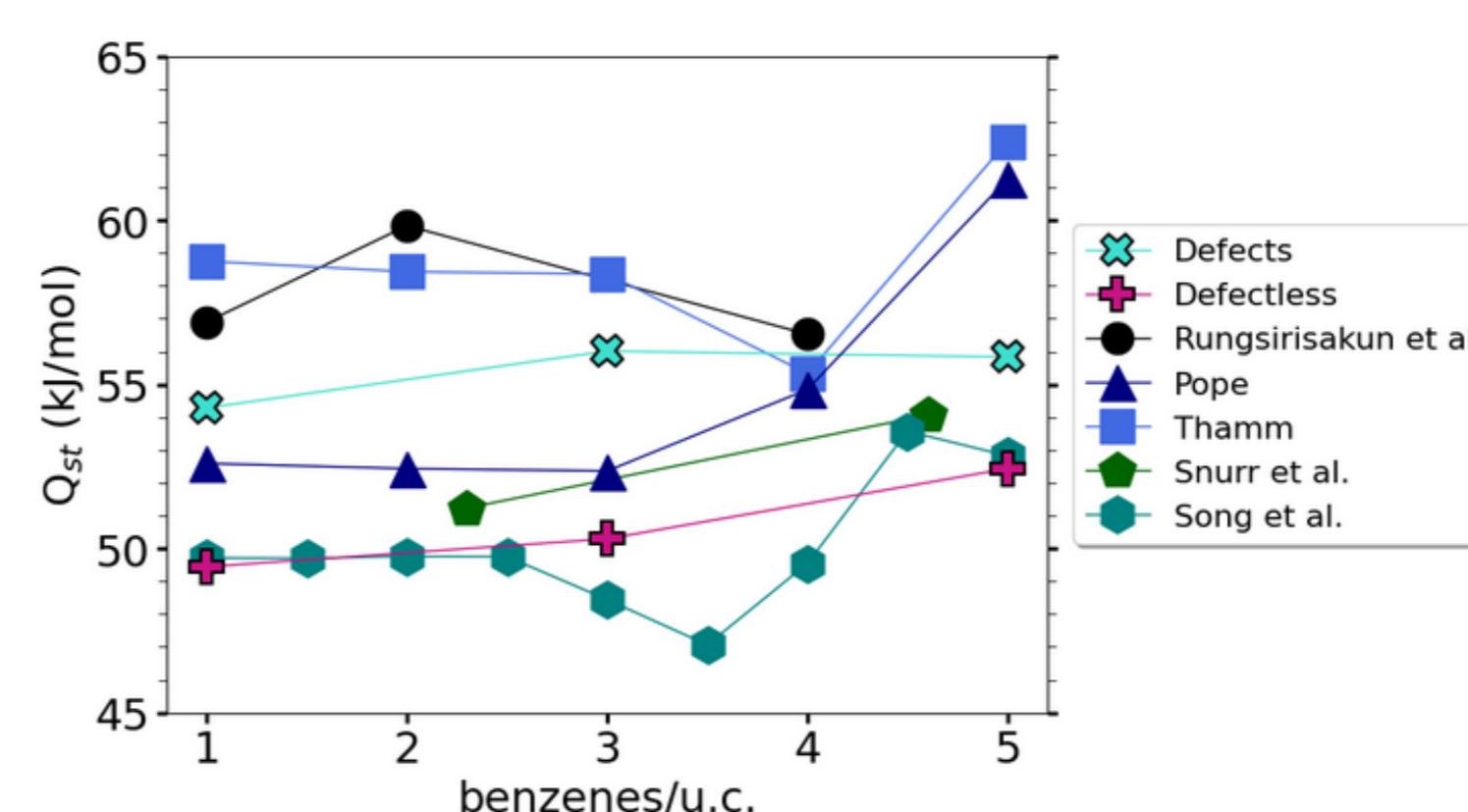

Figure 2: Calculated and experimental heat of adsorption (Q_{st}) of benzene in pure silica MFI (silicalite) at different loadings.

Our results indicate for the defectless zeolite a close agreement to the experimental results A neat effect of increase, of **3.4-5.7** kJ/mol, in our calculated heat of adsorption is observed when changing from the defectless ZSM-5 to the structure with defects. This is due to the specific interactions of the silanol groups with the benzene molecule as well as the structural silicalite deformation induced by the silanol defects.

Self-diffusivity

Self-diffusion coefficients obtained (Figure 3) allow to assess the effects of loading, temperature and structural defects, and are also compared to experimental results in the literature.

Unfortunately, our results are between one and two orders of magnitude larger than those obtained from experiments. Since the heats of adsorption are in good agreement with experiments, the reason why self-diffusivities are so large must be found in the values of zeolite···benzene interactions in the less attractive region of the diffusion path.
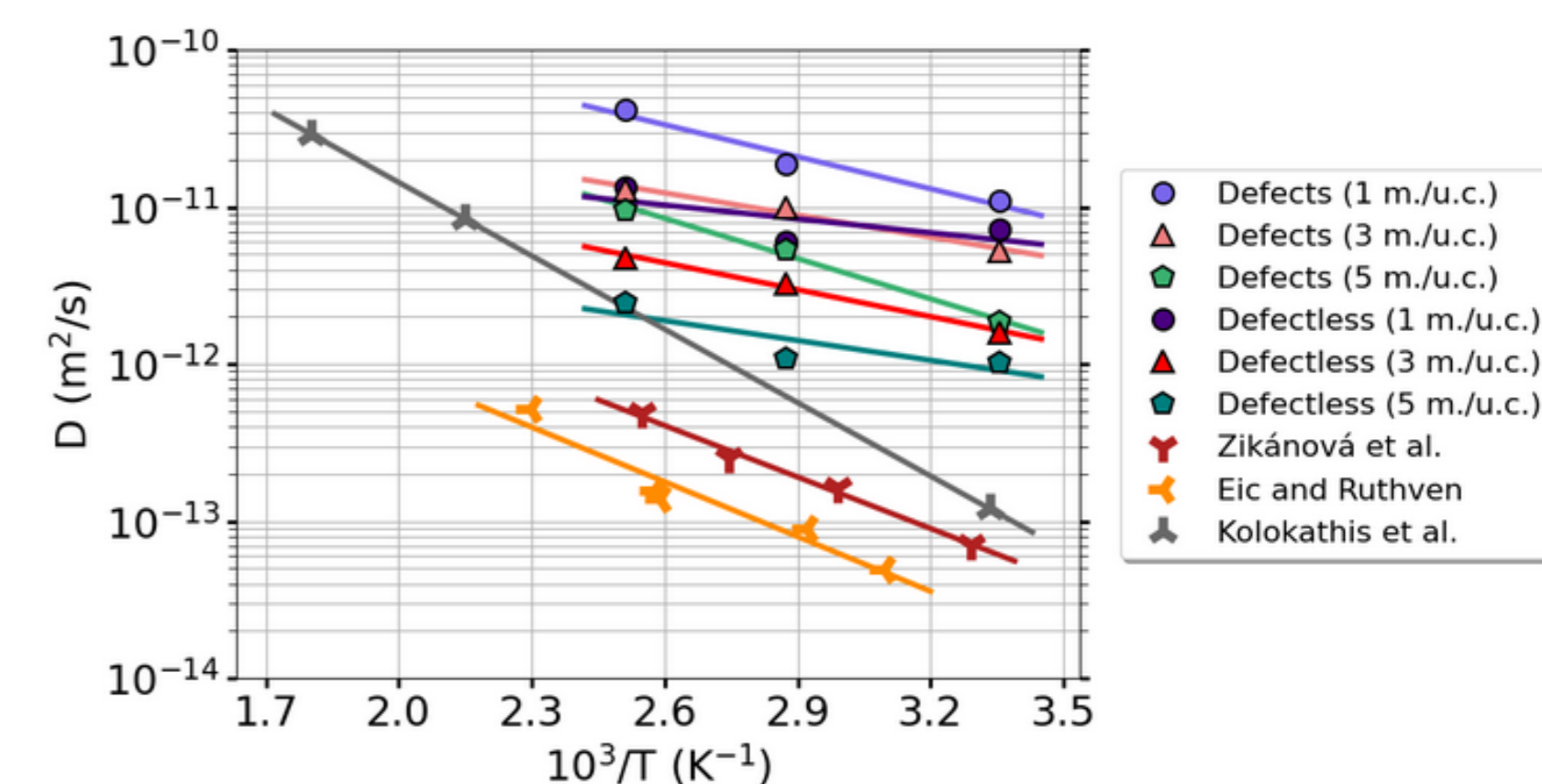

Figure 3: Arrhenius plot for diffusion of benzene in silicalite. Simulated self-diffusion coefficients (D) for framework with defects and defectless, with different benzene loadings (molecules per unit cell).

Defect healing reaction

The proposed silanol condensation reaction mechanism follows a concerted Transition State (TS) in which a silanol protonates a neighboring silanol, while a Si-O bond is being formed, as can be seen on Figure 4.
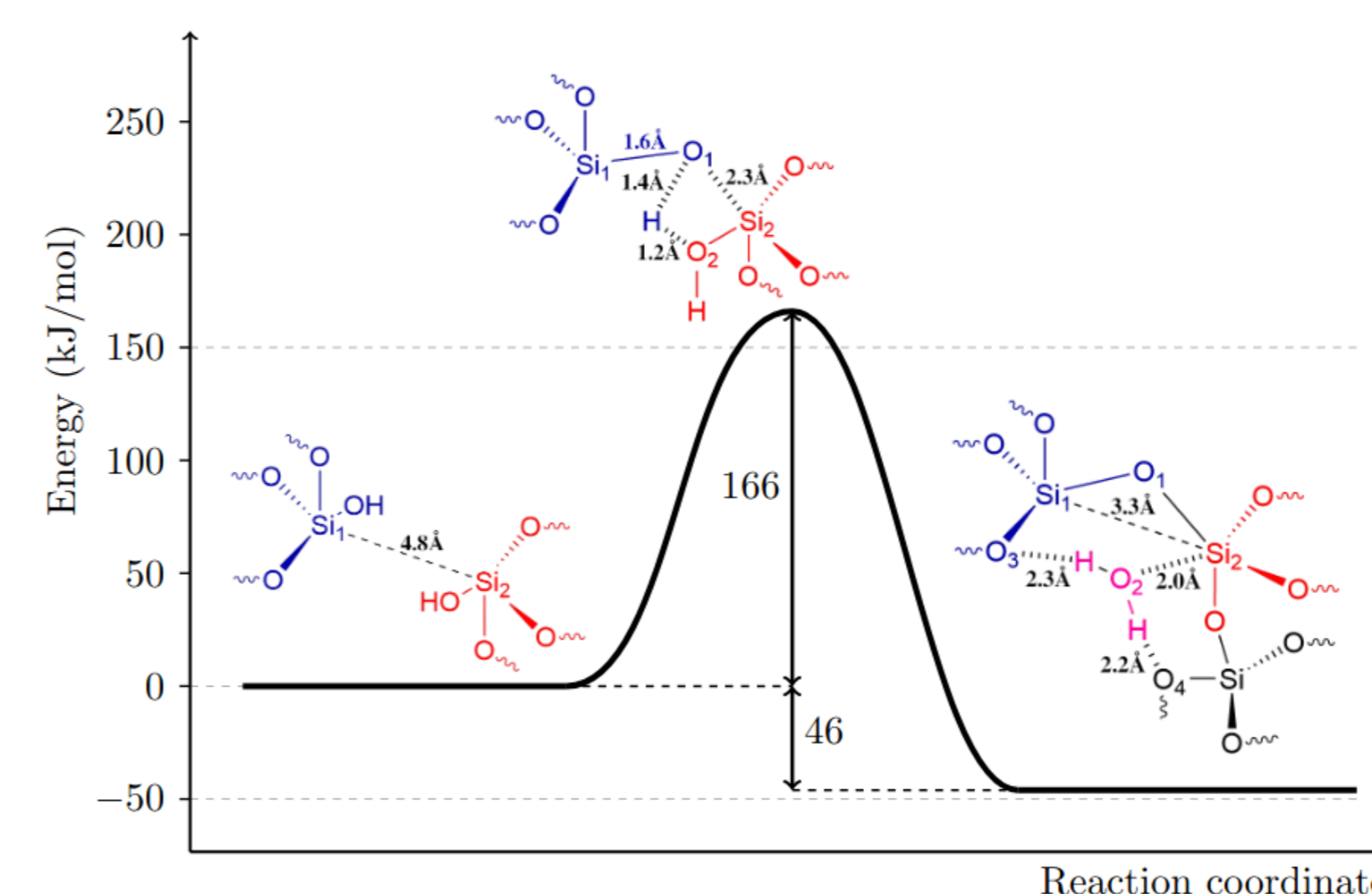

Figure 4: Scheme of the silanol condensation reaction ($2\equiv SiOH \rightarrow \equiv SiOSi\equiv + H_2O$), showing the relevant distances of: reactants, TS, and products.

The deprotonated silanol (siloxy), Si-O-, then forms the Si-O-Si bond (thus repairing the defect) while the formed H_2O molecule remains adsorbed to the zeolite. This reaction shows an "early" TS in which the proton is transferred between silanols, and the siloxy group formed is just beginning to form a Si-O-Si linkage. This TS has an activation energy of **166** kJ/mol with respect to the initial energy of the reactants. The overall reaction is exergonic by **-46** kJ/mol, in agreement to the early TS observed, and hence the reverse hydrolysis reaction has a larger activation barrier, of **166+46 = 212** kJ/mol.

Conclusions

- The computed heats of adsorption are in good agreement with experimental values.
- Self-diffusivity of benzene in silicalite is 2.5 times larger in the structure with defects compared to the "defectless" zeolite, assessed to a slightly larger micropore space available due to the fact that defects tend to protrude outside the micropore.
- The silanol condensation reaction has been evaluated, giving a rational reaction pathway.

Work applicability

This works shows the potential effect diffusion events have on the general reagent mobility inside the zeolite framework, which can greatly influence catalytic processes.

References

(1) Misturini, A.; Rey, F.; Sastre, G. *The Journal of Physical Chemistry C* **2022**, *126*, 17680–17691.
(2) Stewart, J. J. P. *Journal of Molecular Modeling* **2013**, *19*, 1–32.

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