

## Diffusion and adsorption of 2-methylpentane and 3-methylpentane in silicalite-1 crystals

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### Introduction

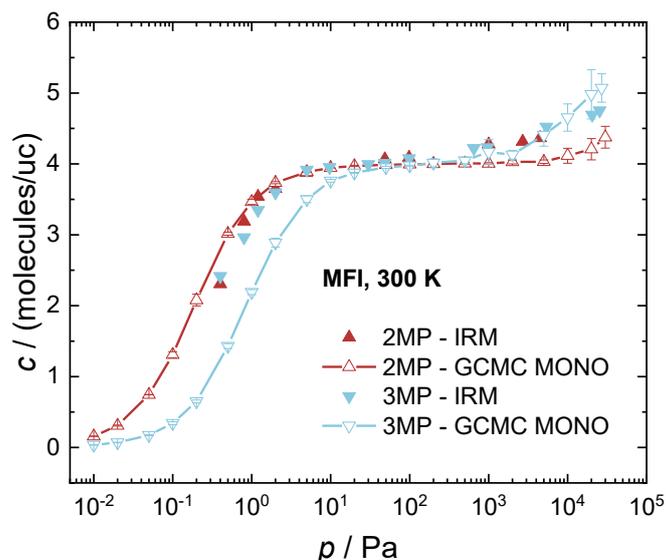
Molecular diffusion is often a key criterion for the performance of microporous materials in technological applications [1]. Due to the intimate contact of guest molecules with the inner surface of microporous adsorbents, slight changes in the structure of the guest molecules may already lead to considerable changes in their diffusion behavior. One example of such behavior, which is investigated in this study, is the diffusion of 2-methylpentane (2MP) and 3-methylpentane (3MP) in large crystallites of silicalite-1 studied via IR microscopy (IRM). Furthermore, a rationalization of the observed large differences (factor of 3) in the transport diffusivity of 2MP and 3MP using both Grand Canonical Monte Carlo (GCMC) and dynamically corrected transition state theory (dcTST) simulations is attempted.

### Experimental

Silicalite-1 was prepared via a synthesis adapted from Mueller and Unger [2] using Ludox® as silica precursor, aqueous ammonia solution as base and tetrapropylammonium as structure-directing agent. The molar composition of the synthesis gel was 59:4:123:2280 ( $\text{SiO}_2/(\text{TPA})_2\text{O}/(\text{NH}_4)_2\text{O}/\text{H}_2\text{O}$ ). Diffusion investigations were conducted with a Bruker Hyperion 3000 IR microscope attached to a Bruker Vertex 80 FT-IR spectrometer with polychromatic MIR source, Michelson Interferometer and a single element MCT (mercury cadmium telluride) detector. Grand canonical Monte Carlo simulations were carried out using the RASPA2 package [3] using force field parameters from Dubbeldam [4] to predict the single component sorption isotherms. To estimate the self-diffusivity of 2MP and 3MP the dynamically corrected TST method was used [5].

### Results and Discussion

The adsorption isotherms in Fig. 1. show that 2MP adsorbs more strongly at loadings  $< 4$  molecules per unit cell while the equilibrium loading is higher for 3MP at loadings  $> 4$  molecules per unit cell. The experimental data obtained is in good agreement with GCMC simulations for silicalite-1 in its monoclinic state. Additionally, the loading dependent transport diffusivities were studied. The transport diffusivity only marginally increases below a loading of 4 molecules per unit cell, but strongly increases for a higher loading in the case of both 2MP and 3MP. While the trend observed for both molecular probes is the same, the transport diffusivity of 2MP is 2.0 – 4.5 times higher than that of 3MP. This is attributed to lower energy barriers for 2MP mobility, differences in the energy profiles and the orientation of both molecules inside the pore system with the help of dcTST simulations.



**Fig. 1.** Adsorption isotherms of 2-methylpentane and 3-methylpentane inside monoclinic silicalite-1 at 300 K, as obtained from IRM experiments and GCMC simulation. The loading  $c$  is given in molecules per unit cell.

## Conclusions

Overall we see a faster hopping rate in the sinusoidal channels of silicalite-1 compared to the straight channels for both molecules. 2MP has a longer carbon backbone compared to 3MP when considering the location of the methyl-branch. The orientation of 2MP inside of an intersection is such that its longer ‘tail’ will be oriented into either a straight or sinusoidal channel, facilitating its jump from one intersection to the next, while 3MP remains more confined within the preferred intersections. As such, the simulation data correlates nicely with our experimental findings.

## References

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