

# Utilization of Structural Flexibility in MOFs for the Separation of Hydrocarbons

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## INTRODUCTION

Flexible gate-opening metal-organic frameworks (GO-MOFs) are known to expand or contract via a phase transition as a response to external stimuli such as temperature, pressure and sorption of guest molecules [1-2]. Since the transition pressures are guest dependent, this dynamic feature could potentially enable the utilization of these materials as adsorbents in gas separation processes [3]. However, experimental data in this field concerning both the thermodynamic

equilibrium and kinetic behavior are still scarce. In this contribution, pure gas and gas mixture adsorption of *n*-butane and *iso*-butane as probe molecules were investigated on the known flexible *paddle-wheel* MOF (1) [Cu<sub>2</sub>(H-Me-trz-ia)<sub>2</sub>] [4]. Therefore, gravimetric isotherms and kinetic measurements were conducted as well as breakthrough curve experiments (BTC) on a fixed bed in order to gain insight into the influence of the phase transition upon competitive adsorption.

## RESULTS AND DISCUSSION

### Pure Gas Adsorption

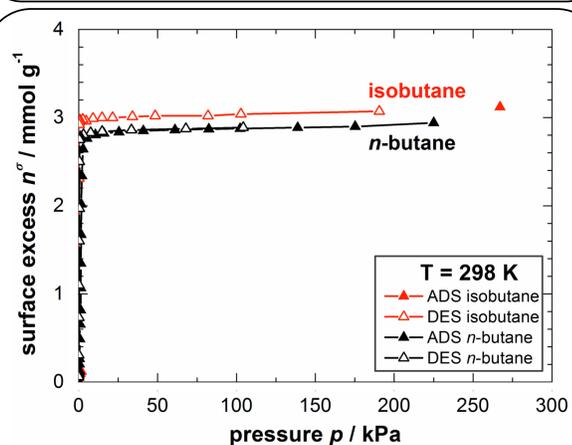


Fig. 1: Pure gas sorption of *n*- and *iso*-butane at 298 K on 1.

### Mixed Gas Adsorption

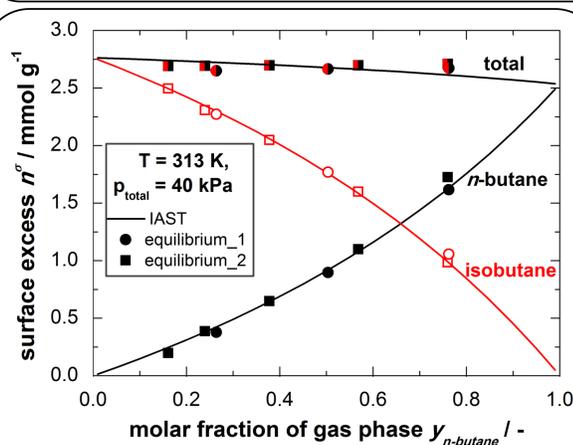


Fig. 2: Plot for partial loadings of *n*- and *iso*-butane on 1 resulting from equilibrated mixture measurements.

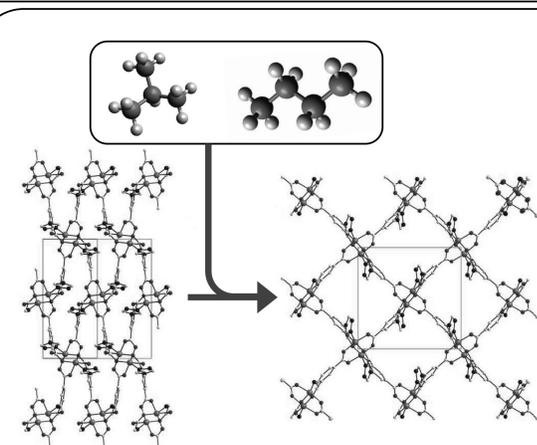


Fig. 3: Illustration of the evacuated and the opened phase of 1.

Equilibrium Measurements

Kinetic Measurements

Dynamic Sorption - BTC

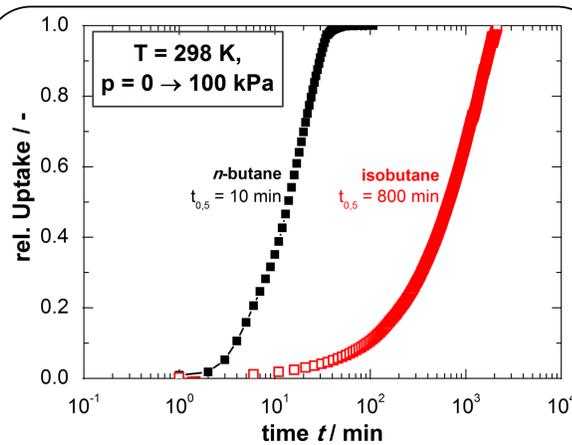


Fig. 4: Uptake curves for pure gas sorption of *n*- and *iso*-butane at 298 K and a pressure step  $p = 0 \rightarrow 100$  kPa on 1.

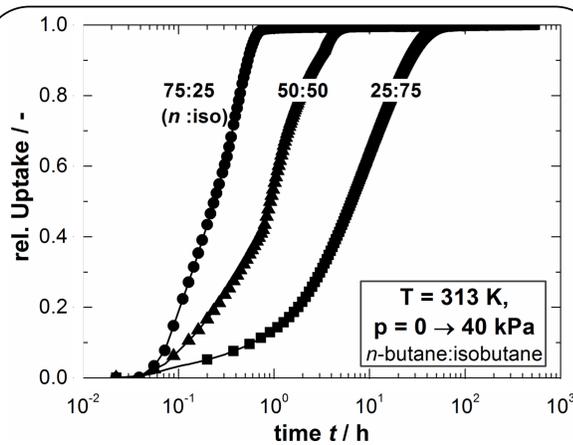


Fig. 5: Uptake curves for mixture gas sorption of *n*- and *iso*-butane at 313 K on 1.

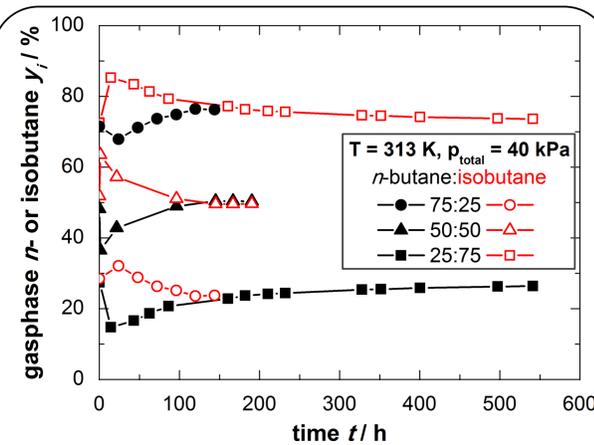


Fig. 6: Shift in gas phase composition regarding *n*-butane (open symbols) and *iso*-butane (closed symbols).

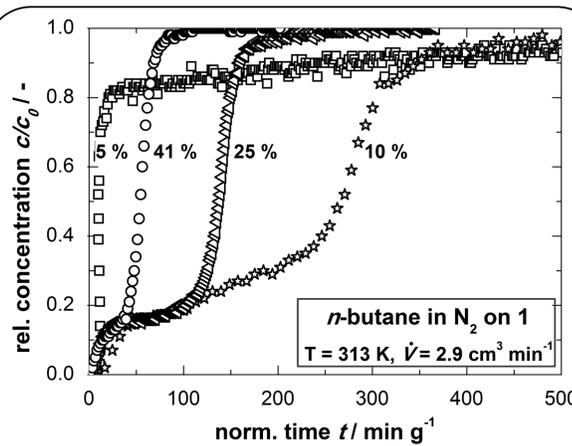


Fig. 7: Breakthrough curves (btc) of *n*-butane ( $x$  % in N<sub>2</sub>, 3 mL min<sup>-1</sup>) on 1 at 313 K.

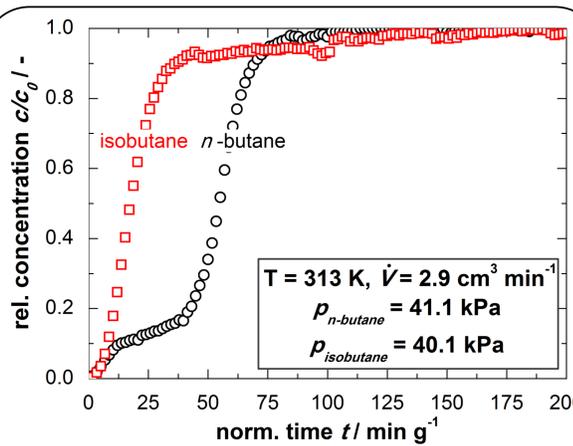


Fig. 8: Comparison of btc for *n*-butane and *iso*-butane on 1 at 313 K.

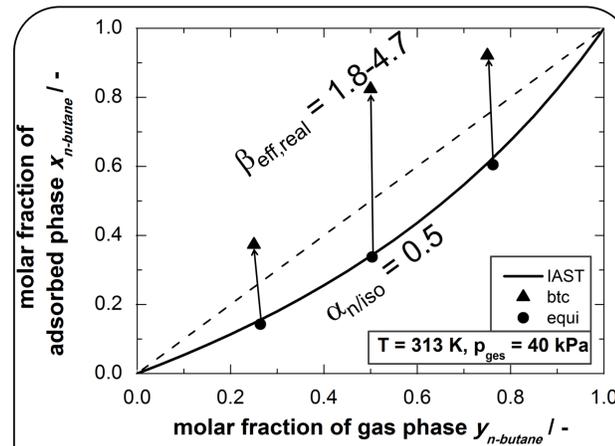


Fig. 9: Molar fractions of *n*-butane by sorption of mixtures incl. the shift in selectivity between equilibrated and btc experiments.

## CONCLUSIONS

- Both *n*-butane and *iso*-butane sorption open the framework under equilibrium conditions with a pore volume of 0.30 cm<sup>3</sup> g<sup>-1</sup> and 0.33 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. 1). As a result, equilibrated static mixture measurements show preferential sorption of *iso*-butane, which is consistent to ideal adsorbed solution theory (IAST) (Fig. 2).
- Kinetics of *n*-butane and *iso*-butane are essentially different: *n*-butane diffuses much faster into the framework (Fig. 4)  $\rightarrow$  material with high kinetic selectivity.
- Dynamic sorption experiments with a packed sorbent bed led to stepwise breakthrough curves (btc) affected by entry concentration of the sorptive (Fig. 7).
- While sorption of *n*-butane partially occurs, *iso*-butane is detected at the adsorber outlet already when starting the experiment (Fig. 8).
- The calculated selectivity ( $\alpha = 0.5$ ) for static equilibrated measurements resembles the enrichment of *iso*-butane in the adsorbed phase. In contrast, from btc the effective, real selectivity  $b_{\text{eff,real}}$  is obtained with values between 1.8 without an framework opening and 4 - 5 including a structural change (Fig. 9).

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