

## Evaluation of the Metal-Organic Frameworks MIL-47, MIL-53 and Cu<sub>3</sub>(BTC)<sub>2</sub> for the Adsorptive Separation of Molecular Mixtures

Vincent FINSY

A new class of microporous adsorbents, the metal-organic frameworks was recently developed. Despite their promising characteristics, not much is known about their adsorption behaviour, certainly for mixtures. In this work, vapour and gas phase adsorption and separation of (i) linear and branched alkanes, cyclohexane and benzene, (ii) C8 alkylaromatic compounds and (iii) CO<sub>2</sub> and CH<sub>4</sub> is studied on three different metal-organic frameworks, MIL-47, MIL-53 and Cu<sub>3</sub>(BTC)<sub>2</sub>. Special attention is devoted to the elucidation of the observed selectivity mechanisms. This work comprises an experimental determination of low coverage adsorption properties using chromatography, isotherms using gravimetry and separation behaviour using breakthrough experiments.

Low coverage adsorption properties of MIL-47, MIL-53 and Cu<sub>3</sub>(BTC)<sub>2</sub> are determined using the pulse gas chromatographic technique. The effect of the nature and accessibility of the cation, pore size and topology on the adsorption properties is determined. Adsorption of linear alkanes at infinite dilution reveals, regardless the large difference in composition between metal-organic frameworks and zeolites, comparable adsorption potentials for zeolites, MIL-53 and MIL-47. The effect of the cations on the adsorption strength is strongly dependent on the type of MOF and is smaller compared to zeolites. Whereas on zeolites, the presence of cations results in higher adsorption strengths for benzene compared to *n*-hexane and cyclohexane, adsorption enthalpies of benzene are smaller compared to *n*-hexane on MIL-47, MIL-53 and Cu<sub>3</sub>(BTC)<sub>2</sub>. On MIL-47 and MIL-53, the adsorption enthalpy of benzene is even smaller than the one of cyclohexane. On Cu<sub>3</sub>(BTC)<sub>2</sub>, the adsorption enthalpy of benzene is larger compared to the one of cyclohexane. Additionally, in context of its pore dimensions, very large adsorption enthalpies of linear alkanes were observed for Cu<sub>3</sub>(BTC)<sub>2</sub>. All metal-organic frameworks preferentially adsorb linear over branched alkanes, but only Cu<sub>3</sub>(BTC)<sub>2</sub> possess true shape selective properties and is able to discriminate dimethylbranched from linear alkanes, solely on the basis of their difference in shape.

In a second part of the work, the potential of MIL-47 and MIL-53 for the adsorptive

separation of mixtures of C8 alkyl aromatic compounds is evaluated. At zero coverage, no selectivity is found for MIL-47. All xylene isomers and ethylbenzene have comparable Henry constants and adsorption enthalpy. Adsorption isotherms of the pure compounds were determined using the gravimetric technique at 70, 110 and 150 °C for MIL-47 and at 110 °C for MIL-53. On MIL-47 the adsorption capacity and isotherm steepness differs amongst the components and are strongly temperature dependent. On MIL-53 the adsorption capacity and isotherm steepness and shape differs amongst components. Breakthrough experiments demonstrate that MIL-47 and MIL-53 materials can be used for the separation of molecular mixtures of xylene isomers. In general, it was found that the adsorption selectivity increases with increasing degree of pore filling. The observed selectivity at high degree of pore filling is the result of differences at which the isomers are packed inside the pores of MIL-47 and MIL-53.

Additionally, the selectivity of MIL-53 is affected by a pore breathing mechanism. The adsorption isotherms of ethylbenzene, o-, m-, and p-xylene show two well-defined steps corresponding to the breathing of the framework. At low concentrations, the adsorption of the C8 alkyl aromatic components induces a contraction of the pores. At higher pressures, the pores are reopened and additional molecules are adsorbed. Together with the opening of the pores, both the molecular sitting and the selectivity mechanism are altered. In the contracted pores, there is only space for a row of single molecules, adsorbed along the length of the pores. In this condition, there is no difference in adsorption between the different components. No separation can be obtained. In the open form of the MIL-53 framework, the space is sufficiently large for the xylene isomers to be adsorbed in pairs along the length of the pores, leading to an increase in the amount adsorbed. Due to differences in the efficiency at which the xylene isomers are packed inside this larger space, differences in the steepness of the isotherms and the adsorption capacity are observed. As a result, separation of molecular mixtures is feasible. Ethylbenzene, in contrast to the xylene isomers, is not able to adsorb in pairs along the length of the open pores leading to a large difference in adsorption capacity compared to the former.

Separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures on MIL-53 is studied by performing breakthrough experiments at 30 °C and varying pressure and mixture composition. Over the whole concentration and pressure range CO<sub>2</sub> is preferentially adsorbed over CH<sub>4</sub>. The adsorption selectivity originates from a difference in adsorption mechanism between CO<sub>2</sub> and CH<sub>4</sub> and

is affected by total pressure. At pressures up to 5 bar, CO<sub>2</sub> interacts very strong with the framework hydroxyl groups. CH<sub>4</sub> in contrast, is not capable of similar interactions and is adsorbed less strongly. In these conditions the selectivity is not influenced by the mixture composition. At higher pressures, the adsorption mechanism of CO<sub>2</sub> is changed. All the specific adsorption sites are occupied and the remaining CO<sub>2</sub> molecules are adsorbed in a non specific way. The overall selectivity between CO<sub>2</sub> and CH<sub>4</sub> decreases. In addition, the adsorption selectivity is influenced by mixture composition. At a pressure of 7.4 bar and from mole fractions of 0.4 the average selectivity decreases with increasing CO<sub>2</sub> concentration. Again a change from strong selective to weaker, non selective adsorption is the cause. At a pressure of 7.4 bar, from CO<sub>2</sub> mole fractions of 0.4, all the specific adsorption sites are occupied and with increasing CO<sub>2</sub> concentration, an ever increasing amount of CO<sub>2</sub> molecules are adsorbed in an unspecific manner.