Anomalous Relationship between Molecular Size and Diffusivity for Ethane and Ethylene Diffusion inside Crystals of Zeolitic Imidazole Framework-11

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Introduction

Zeolitic imidazolate frameworks (ZIFs) has seen recent interest as promising microporous materials for gas separations, including paraffin/olefin separations. ZIFs consist of metal ions or clusters interconnected by organic linkers. In particular, ZIF-11 has attracted attention due to its small crystallographic pore aperture size of 3.0 Å, giving ZIF-11 appropriate structural characteristics for molecular sieving of small gas molecules. Our recent pulsed field gradient (PFG) NMR study demonstrates that confinement of ZIF-11 crystals in a polymer can lead to a reduction of self-diffusivity of ethylene molecules inside the crystals [1]. A tentative explanation for this effect has been that confinement of the ZIF-11 crystals in a polymer can lead to a reduced flexibility of the ZIF framework. In this project the role of the framework flexibility is further explored by PFG NMR studies of mixed and pure ethane and ethylene in ZIF-11.

Experimental

^{13}C and ^{1}H PFG NMR at 17.6 and 14 T was used to study self-diffusion of mixed and pure ethane and ethylene in ZIF-11 at different temperatures and gas loadings.

Results and Discussion

PFG NMR diffusion studies of ZIF-11 loaded with a single sorbate showed a larger intracrystalline diffusivity for ethane than ethylene under the same or comparable experimental conditions (Fig. 1), an unexpected result due to the larger size of ethane compared to ethylene. PFG NMR studies also revealed that substituting a fraction of ethane molecules by ethylene decreases intracrystalline diffusivity of ethane (Fig. 1). These results in combination with an observation of a stronger temperature dependence and, as a result, higher activation energy of intracrystalline diffusion for ethylene than for ethane (Fig. 2) suggest a hindering effect of ethylene molecules on the intra-ZIF diffusion.

Conclusions

The diffusion data can be explained by the hypothesis that owing to the ZIF-11 framework flexibility ethylene/framework interaction can reduce the effective aperture size in ZIF-11.

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida.

We are grateful for the financial support of this work by NSF (CBET-1510411 and 1510442) and by the external user program of the NHMFL (project P17444).

References

[1] Forman, E.M., *et al*., Microporous and Mesoporous Materials **274**, 163-170 (2019).

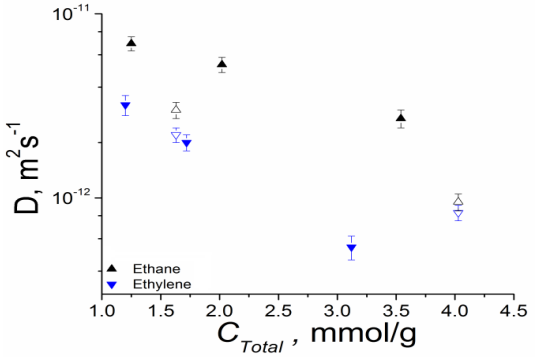

Fig.1 Diffusivities of ethane and ethylene measured in ZIF-11 beds for the smallest diffusion times at 296 K as a function of total sorbate concentration of ethane and ethylene in ZIF-11 crystals. Filled and hollow symbols show data for the single sorbate and mixed sorbate samples, respectively

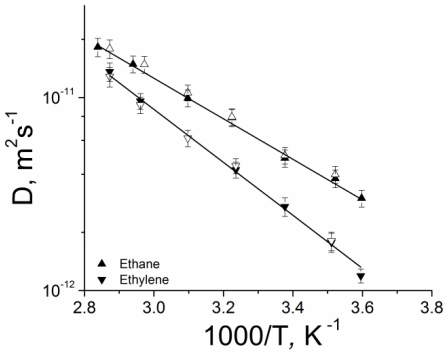

Fig.2 Temperature dependence of intra-ZIF diffusivities of ethane and ethylene under the conditions of the same or similar intra-ZIF concentrations. The measurements were performed using ^{1}H (filled symbols) and ^{13}C (hollow symbols) PFG NMR.