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Transport of light gases across single-crystal zeolite (MOF) nanomembranes: effect of size, flexibility, and polymer coating

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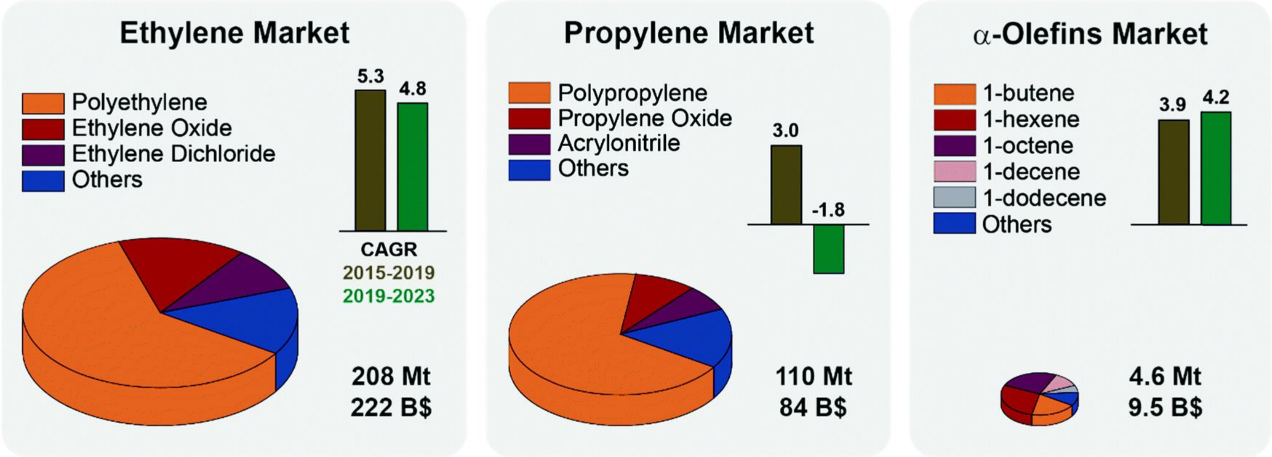
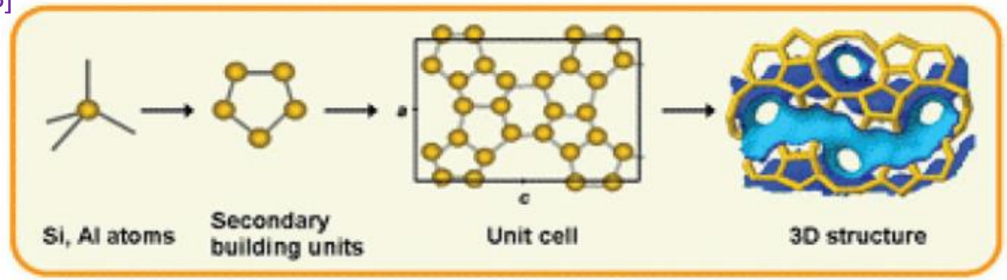
pawsey

Motivation

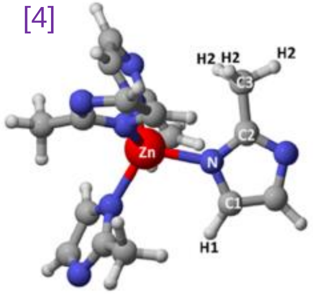
[1]



Zeolites [3]



MOFs [4]



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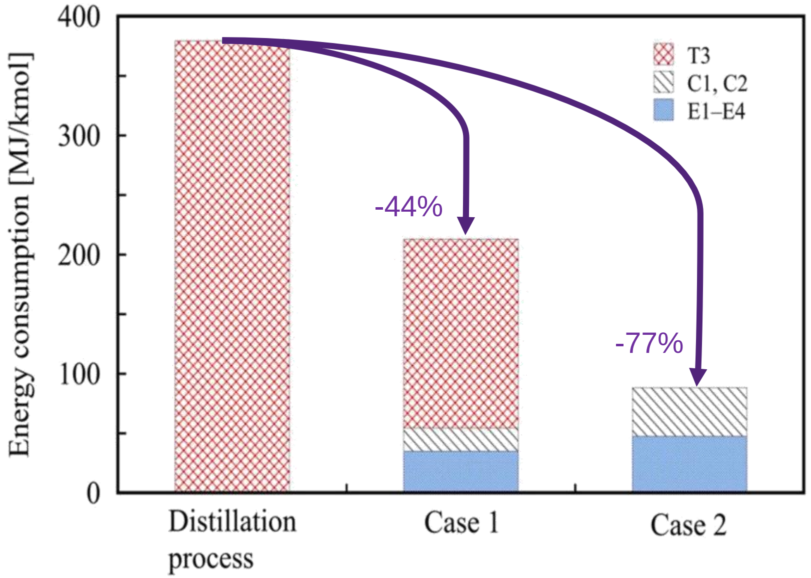
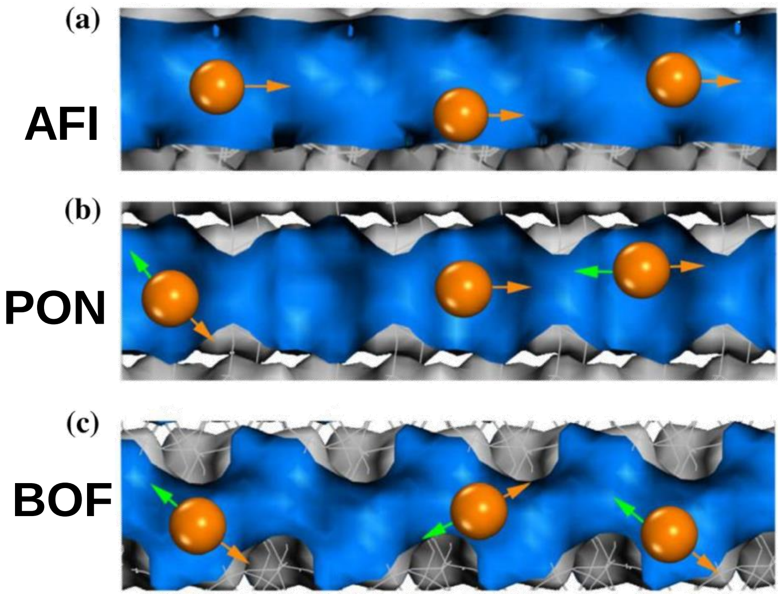
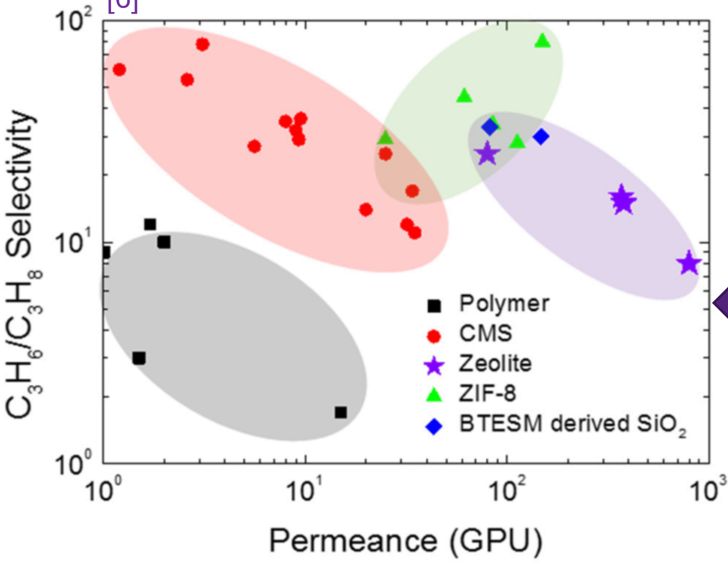


[5]



[6]



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[5] Liu, Z. et al. *AIChE J.* **2020**, *66* (8), 1–4.
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Finite-sized systems

Diffusion Coefficient Estimation

Level of detail

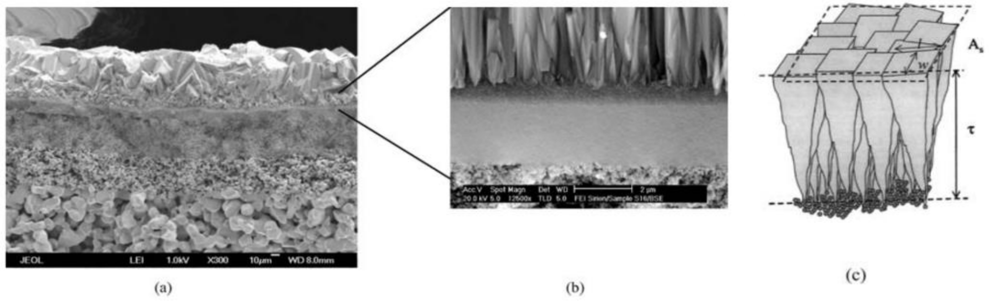
Macro
- ❖ Gravimetric uptake
- ❖ Zero length column (ZLC)
- ❖ Frequency response (FR)
- ❖ Permeation experiments

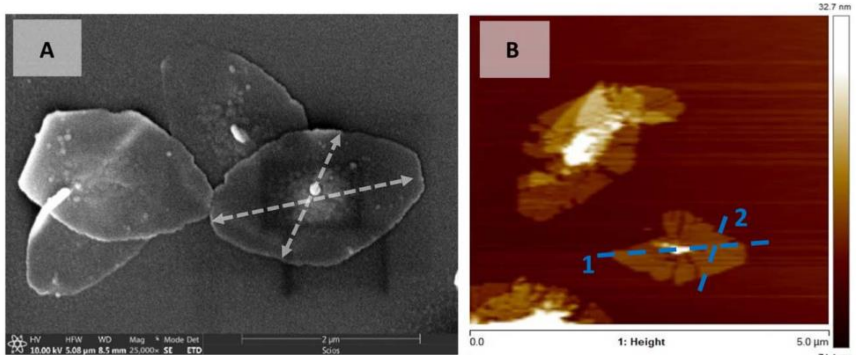
Meso
- ❖ IR Micro-imaging (IRM)

Micro
- ❖ PFG – NMR
- ❖ QENS

What is the origin of the transport barriers in <u>defect-free</u> nanomaterials?

Polycrystalline [8]



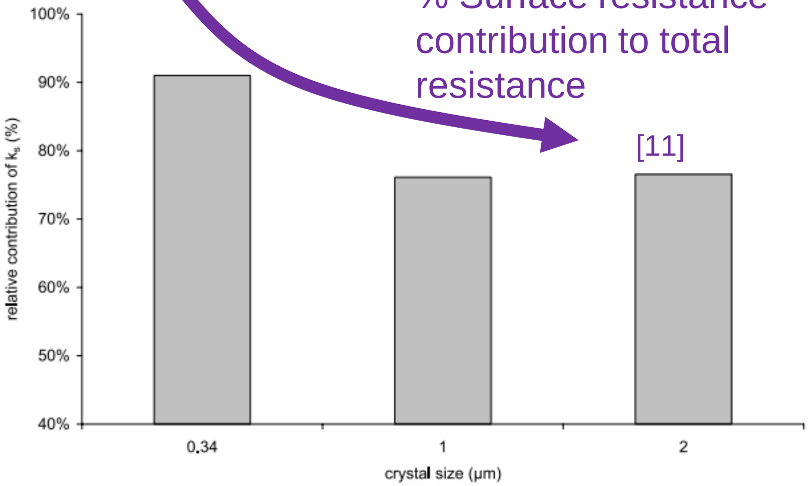


[9]

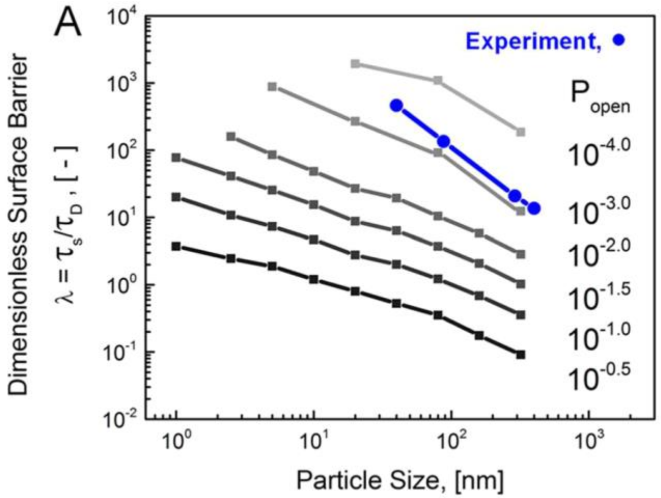
Ultrathin Single-Crystal (Nanosheet)

% Surface resistance contribution to total resistance

[11]



[10]



Open Pores
0.01%
0.1%
1%
3%
10%
31%

Is surface resistance only attributed to pore blocking?

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[9] Cao et al. *Sci. Adv.* **2018**, 4(11), eaau8634.
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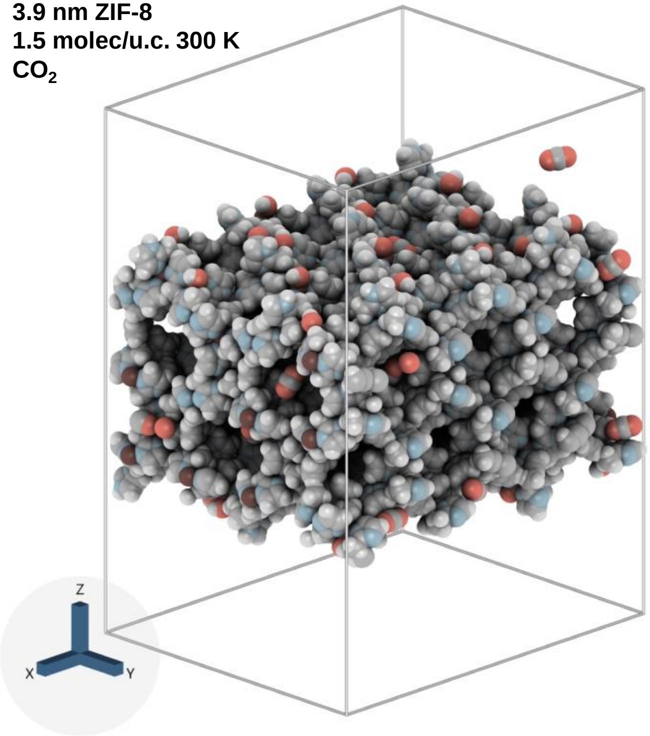
Simulation Details

NVT-MD
3.9 nm ZIF-8
1.5 molec/u.c. 300 K
CO_2



Finite

$$dn = \sum_{S(t)} \frac{dz_i}{L_t} \qquad D_0 = \frac{D_n L}{\rho A_c} = \frac{D_n L^2}{\langle N_{mol} \rangle}$$

Infinite

$$D_{0,\infty} = \frac{N_\infty}{2d} \lim_{t\to\infty} \frac{1}{t} \left\langle \left| \Delta z_{com} \right|^2 \right\rangle$$

GAS

Rigid Force Field
(Gas/Gas)
(Gas/Solid)

$$V_{ij} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

UA
- CH_4, C_2H_6, C_2H_4 **(TraPPE)** [12]
- CF_4, H_2, Ne

AA
- CO_2 (EPM2) [13]

ZEOLITE

Flexible Force Field
(Solid/Solid) [14, 15]

$$V_{ij} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \left[\frac{A_{ij}}{r_{ij}^{9}} + \frac{B_{ij}}{r_{ij}^{6}}\right] + V_{ij}^{bonded}$$

- **PON**
- **MFI**
- **SAS**
- **TON**

MOF

Flexible Force Field
(Solid/Solid) [17, 18]

$$V_{ij} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + V_{ij}^{bonded}$$

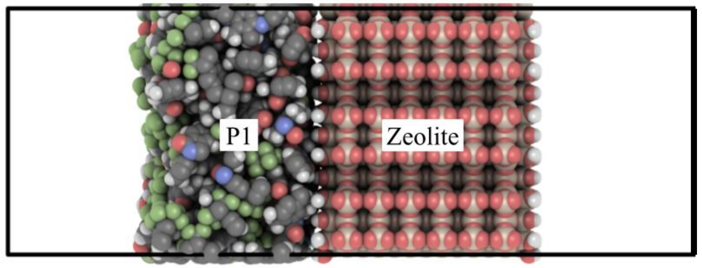
- **ZIF-8**

POLYMER

Flexible Force Field
(Solid/Solid) [19]

$$V_{ij} = \epsilon_{ij}\left[2\left(\frac{r_{\min ij}}{r_{ij}}\right)^{9} - 3\left(\frac{r_{\min ij}}{r_{ij}}\right)^{6}\right] + V_{ij}^{bonded}$$

- **6FDA-Durene polyimide**



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[13] Harris & Yung, *J. Phys. Chem.* **1995**, *99* (31), 12021–12024.
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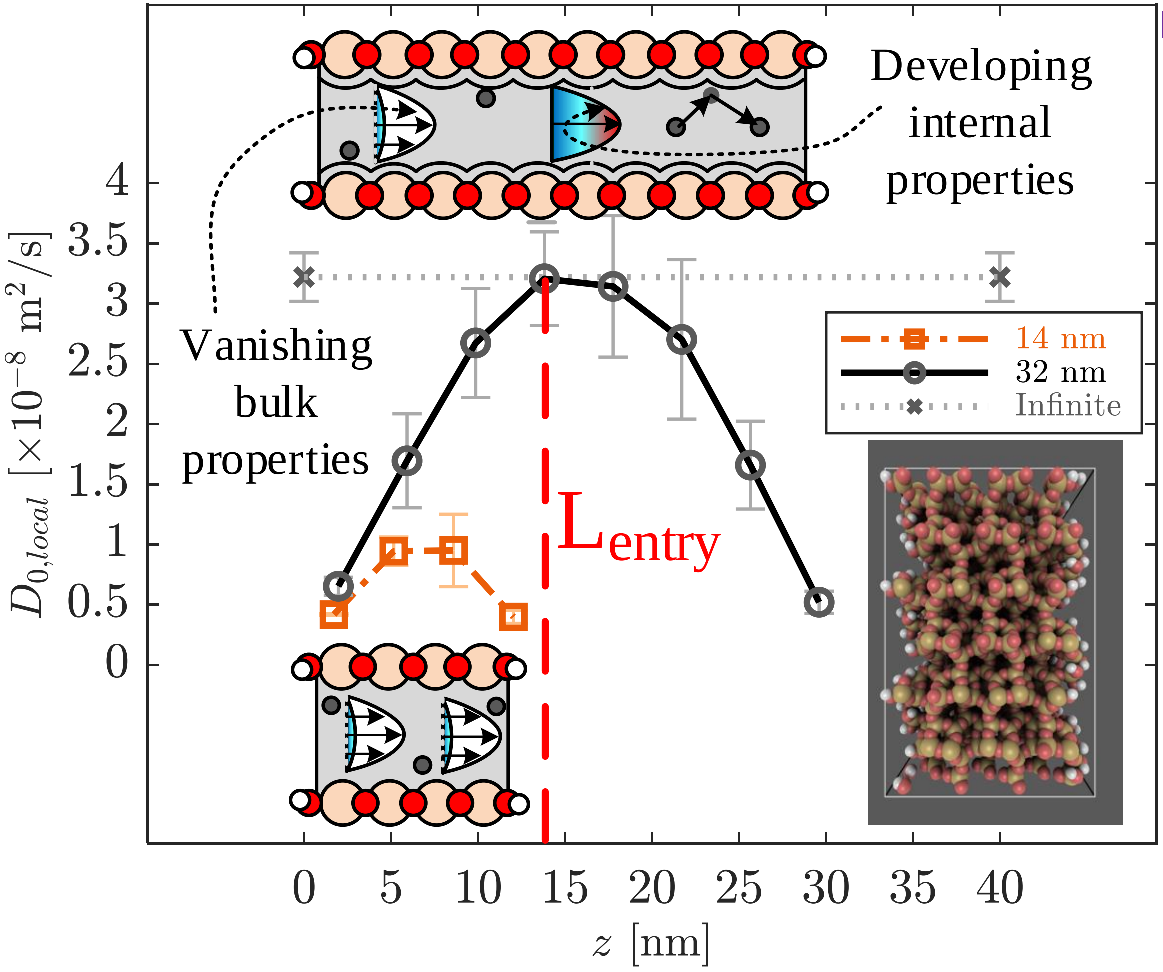
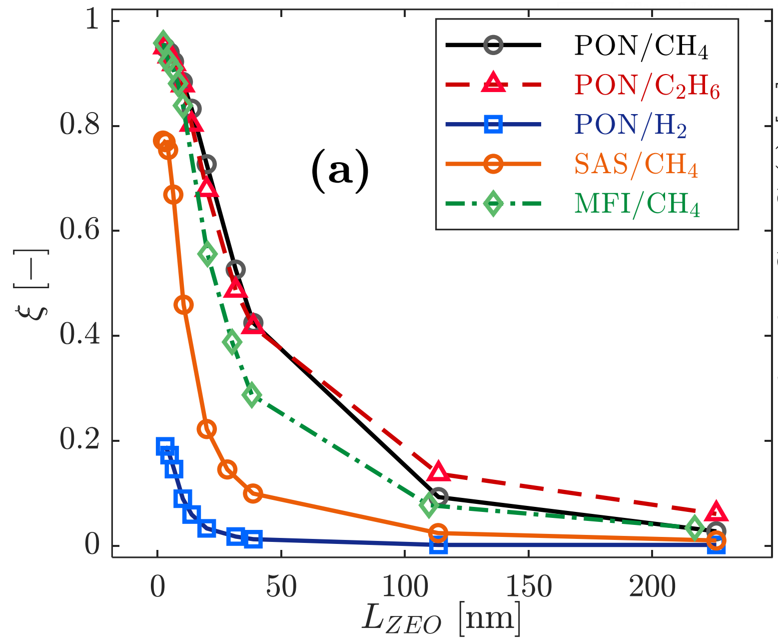
Results: Entry length



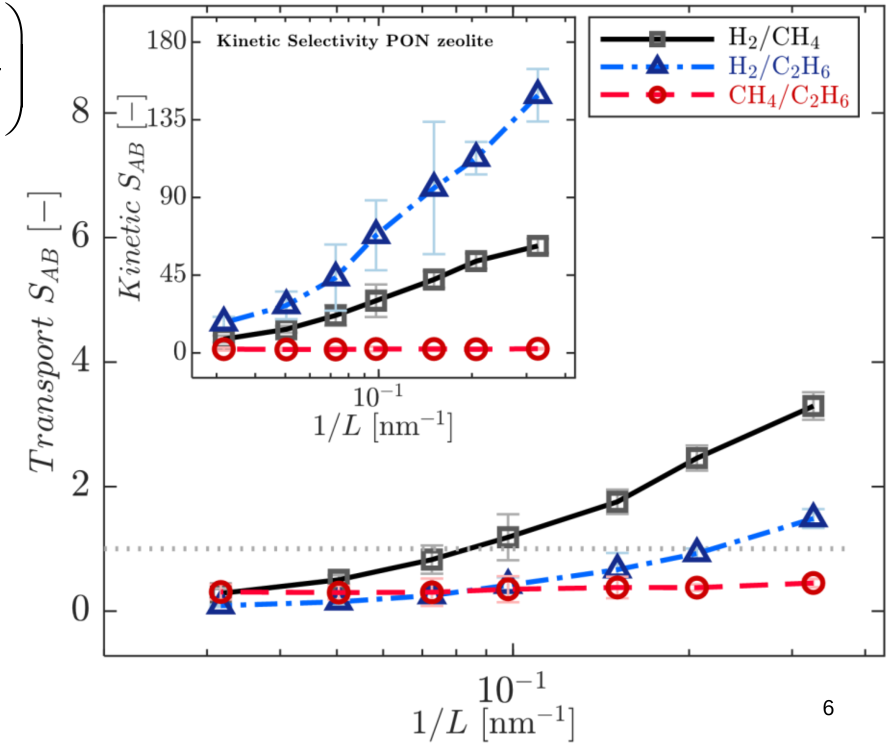
[20]

$$\xi = 1 - \frac{D_0}{D_{0,\infty}}$$



[20]

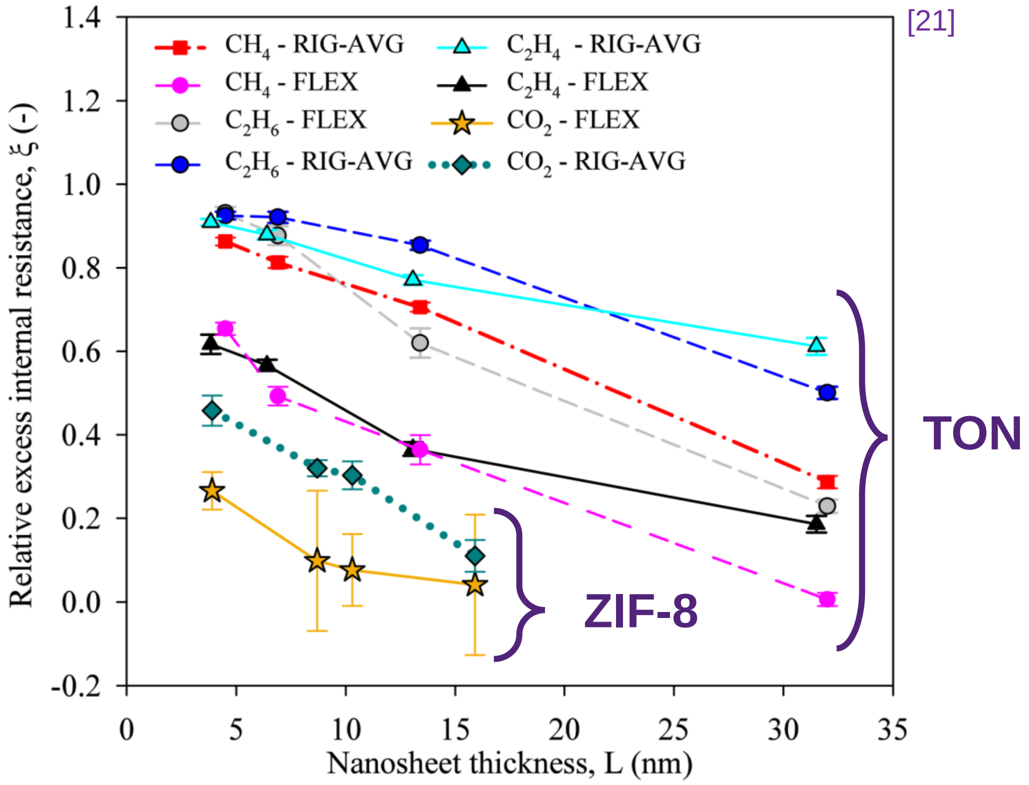
$$S_{AB} = \frac{K_{H,A}}{K_{H,B}}\left(\frac{D_{0,A}}{D_{0,B}}\right)$$

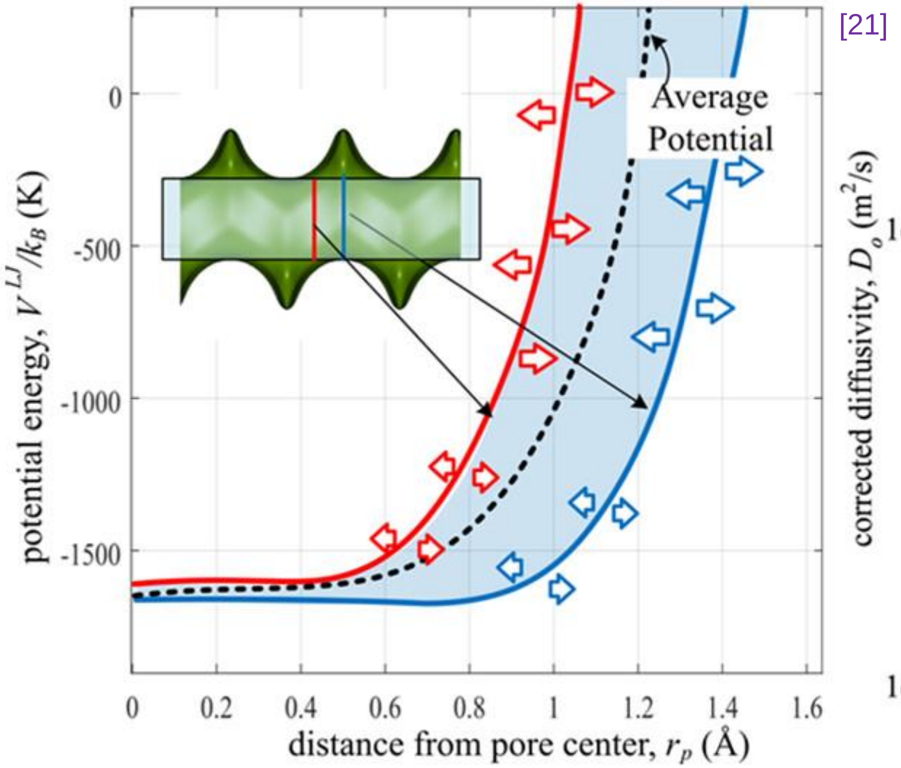


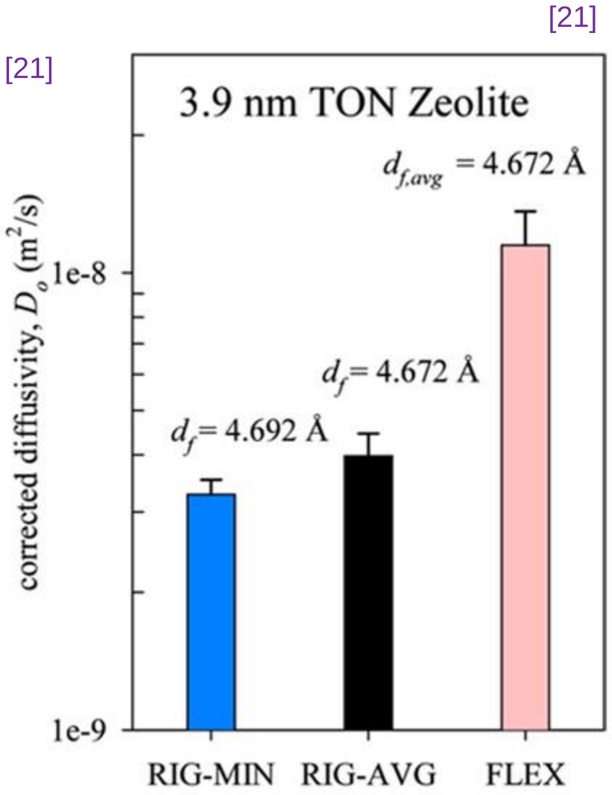
[20]

[20] Zuluaga-Bedoya, Dutta & Bhatia, *ACS Appl. Mater. Interfaces* **2021,** 13(49), 59546-59559.
** Bhatia & Dutta. *J. Phys. Chem. C* **2023**, 127(4), 2035-2044.

Results: Host-Framework Flexibility







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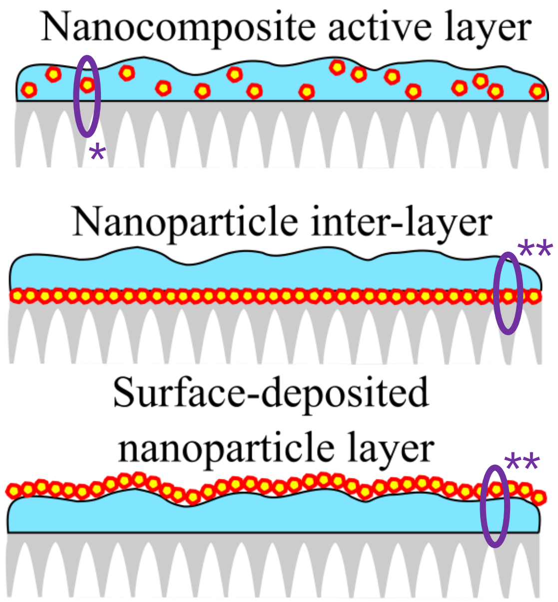
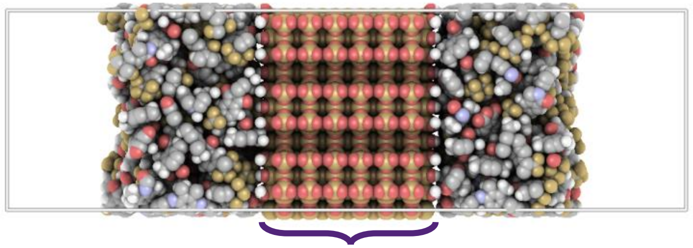
Results: Polymer Coating/Support

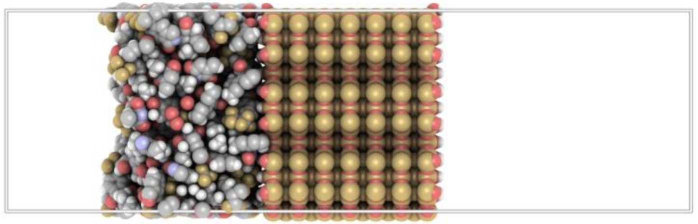


*Double-layered polymeric ZN (COAT)

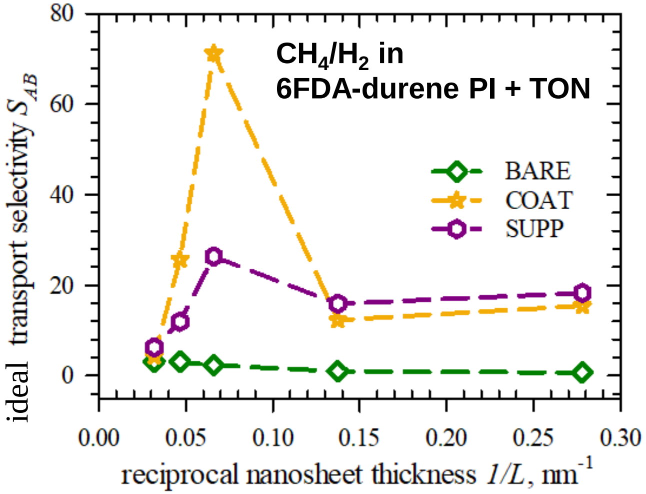


D_o, K_H, L

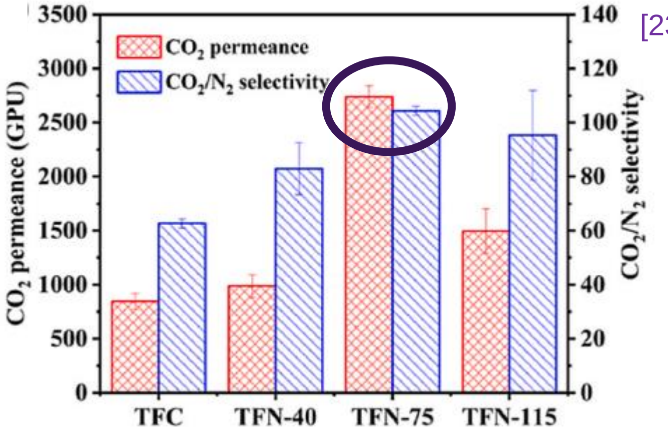
**Single-layered polymeric ZN (SUPP)



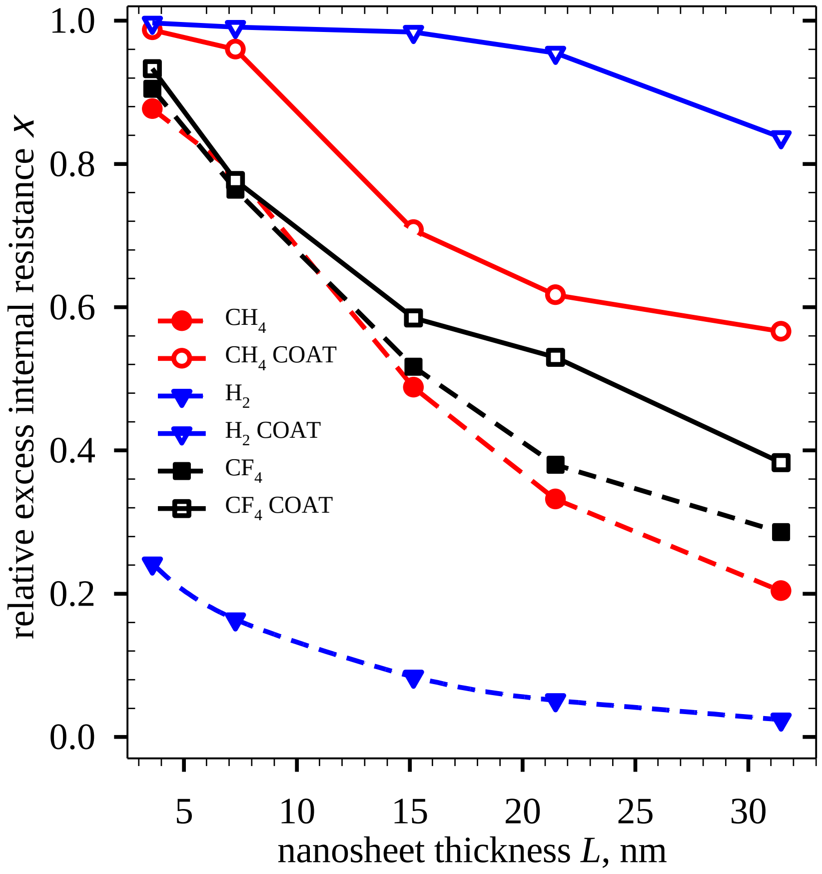
[22]



[23]



[22]



Ne on COAT

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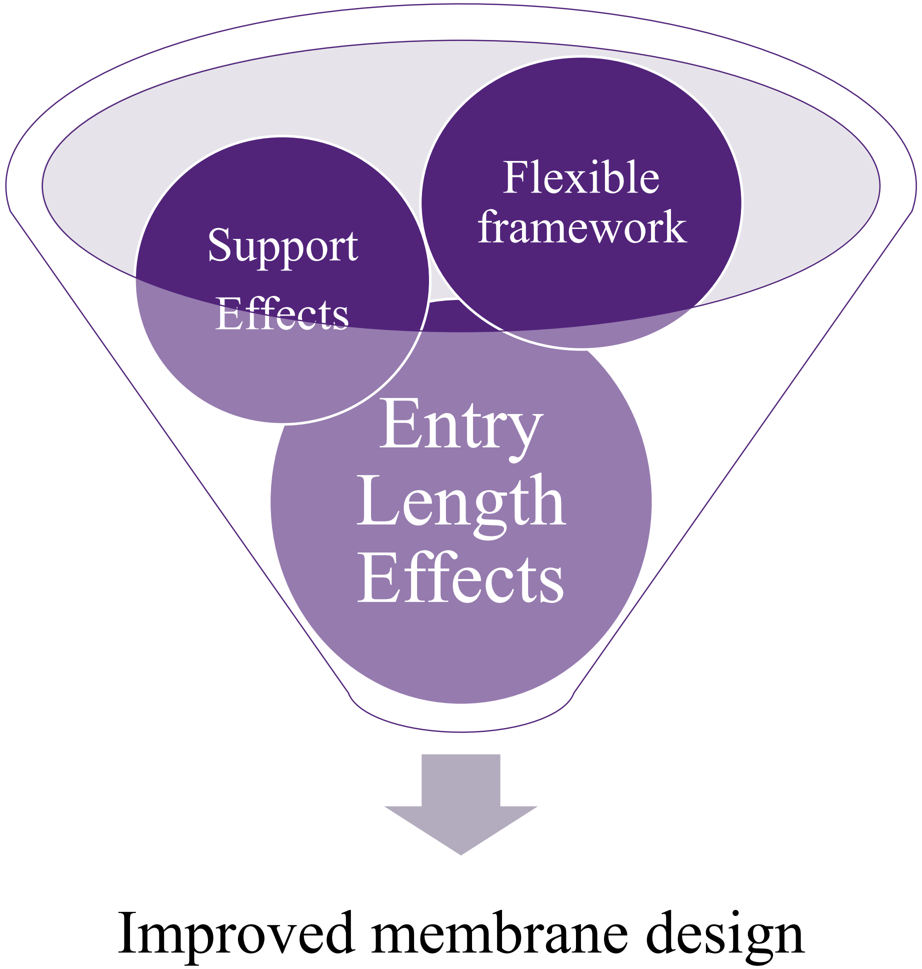
Conclusion



- Transport in **<u>Finite</u>** Crystals $\neq$ Transport in Bulk Crystals
- **<u>Entry length</u>** = Transport Barriers
- Increased Do in for **<u>Flexible Nanosheets</u>** (despite same average d_f)
- Polymer layers decrease $D_{o,ZEO}$ for small molecules = High Transport Barriers
- Polymer layers **<u>increase selectivity</u>** (**<u>optimal</u>** crystal size)

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Thank you

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School of Chemical Engineering

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“The infinite we shall do right away. The finite may take a little longer.”

Stanislaw Ulam