Continuous Zeolite MFI membranes from 2D MFI Nanosheets on Ceramic Hollow Fibers: Fabrication Processes and Hydrocarbon Separation Properties

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High-aspect-ratio 2D zeolite nanosheets for membrane applications

- 2D zeolite nanosheets with high aspect ratio and flexibility
- Preferred orientation and reduced thickness of MFI zeolite membranes

Thin and oriented membrane

High flux and high p-xylene selectivity

Reference work
Jeon MY, et al., Nature 2017 (543), 690-694
Key challenges and motivation

• **2D MFI membrane technology faces challenge of scalability**
  
  Current demonstration of 2D MFI membranes is only possible on small ceramic disks, and requires multiple steps using specialty silica materials

**Scale-up**

• Low-cost, scalable, robust membrane supports needed
• Hollow fiber membranes desirable (> 1000 m²/m³)
• Simple and scalable coating method needed

**Quality**

• Preparation of defect-free nanosheet coatings
• Sealing the non-selective gaps between the nanosheets
• Improve adhesion between nanosheets and the support
• Maintain $b (0k0)$ out-of-plane orientation of pore channels
### Topics in this talk

1. **2D MFI Membrane synthesis and characterizations of microstructures**
   - 2D MFI nanosheet coatings on hollow fibers
   - Sequential macro/nanoscale gap sealing via hydrothermal treatments

2. **Assessment of membrane quality with separation properties**
   - Molecular sieving separation of butane isomer

3. **Extending the applications to removal of C\textsubscript{2+} hydrocarbon from methane**
   - Adsorption dominated separation
   - Multicomponent mixture separation
   - Pressure dependence

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3: B. Min, et al., In preparation
2D MFI membranes on hollow fibers: our fabrication process

- Alumina hollow fiber support
- 2D MFI nanosheets coating
- Continuous oriented, thin MFI film

i. MFI nanosheets coating
ii. (TPA + F) Secondary growth
iii. (TEA) Tertiary growth
Characterizations of 2D MFI nanosheets

~0.5 nm MFI pores are visible

High-aspect-ratio

MFI characteristic XRD patterns

(a) SEM
(b) Electron diffraction pattern
(c) HRTEM
(d) TEM

Randomly packed MFI nanosheets
Simulated MFI
Uniform 2D MFI nanosheet coatings on hollow fibers

**Top View**

**Side View**

**Bare fiber support**

- Dense, uniform coating
- ~ 500 nm thin
MFI membrane synthesis for maintaining \(b\)-orientation

Key Idea: Exploit differences in anisotropic crystal growth seen in TPA-Fluoride and TEAOH media

**Tetrapropylammonium (TPA) hydroxide media**
- Irregular surface
- Abundant twinning and secondary nucleation

**TPA-Fluoride or Tetraethylammonium (TEA) hydroxide media**
- Smooth and flat crystals
- Delay nucleation and suppress surface roughening
- In-plane growth rate can be faster

Selective sealing of microscale/nanoscale gaps by sequential hydrothermal treatments

Top View

Side View

2\textsuperscript{nd} growth: TPA fluoride media
- Selectively sealed the gaps without much overgrowth

3\textsuperscript{rd} growth: TEAOH media
- Laterally well-intergrown
- Final closure of small defects
- Good adhesion
Pore orientation: XRD pattern at each stage

- Strong (0k0) peaks correspond to out-of-plane pore orientation
- TPA-Fluoride and TEAOH treatments are effective for preserving the (0k0) peak
Quantification of pore orientation and thickness changes at each stage

TPA-Fluoride and TEAOH media growth effectively preserves out-of-plane pore orientation while maintaining low membrane thickness (< 1 µm)

Gradual Interpenetration with the support (better adhesion): 2D coating layer < 2nd growth < 3rd growth
Butane isomer separation provides good indication of the membrane quality

- Higher intracrystalline diffusivity of $n$-butane
- $n$-butane: petrochemical feedstock, blending with propane or gasoline
- $i$-butane: refinery feedstock, petrochemical feedstock
Tertiary growth showed high permeance (~ 400 GPU) and high selectivity (~ 42)

- Fluoride media intergrowth produces highly $b$-oriented high flux selective membrane
- Additional intergrowth by TEAOH silica sol reduces non-selective transport pathways
- Reduction in permeance can be minimized by twinning-free intergrowth
Single-component permeation data: a cleaner indication of microstructural quality

- Single-component \( n \)-butane permeances and selectivities are considerably higher than binary values
  - \( i \)-butane competes to a certain extent with \( n \)-butane for permeation in the straight channels of MFI
  - The difference is much more pronounced after tertiary growth than secondary growth: indication of high quality intergrown film with less defects
Removal of C\textsubscript{2-4} hydrocarbons from methane

‘Dry’ natural gas contains mostly methane and a small amount of other hydrocarbons

‘Wet’ natural gas possesses higher amounts of alkanes like propane, butanes and pentanes

- $n$-\text{C}_4\text{H}_{10} (< 11 \%), \text{C}_3\text{H}_8 (< 20 \%), \text{C}_2\text{H}_6 (< 25 \%)$ at ambient temperature

- To reduce soot and coke formation if the gas is used as fuel
- To avoid problems with condensing liquids if the gas is to be compressed and transported in pipelines (max $C_3+$ content of 4.5\% at ambient conditions)
- To increase the methane number
- The higher hydrocarbons also have commercial value if separated
Removal of hydrocarbons from natural gas: adsorption-dominated separation in MFI membranes

Some hydrocarbons present in “wet” natural gas

- Smaller than MFI pore size
- Molecular sieving is not applicable

- Adsorption enthalpy increases as length of the carbon chain of the alkane increases

- Adsorption-dominated separation is possible

Bakker W. J. W., et al., AIChE Journal. 1997 (43) 9, 2203-2214
Separation performance of MFI membranes for quaternary mixture: pressure dependence

**Feed composition** \( n-C_4H_{10} / C_3H_8 / C_2H_6 / CH_4 \ (8/8/8/76) \)

- Permeance decreases with increasing feed pressure
  - characteristic for microporous diffusion
  - negligible amount of high-pressure induced defects in the membrane
- Promising for butane, propane, and ethane removal from methane
Comparison of permeation properties at different feed compositions

1) **Binary** \(n-C_4H_{10}/CH_4\) (10/90), \(C_3H_8/CH_4\) (10/90)
2) **Ternary** \(n-C_4H_{10}/C_3H_8/CH_4\) (9/9/82)
3) **Quaternary** \(n-C_4H_{10}/C_3H_8/C_2H_6/CH_4\) (8/8/8/76)

- A significant reduction in permeance of \(C_3H_8\) in the presence of \(n-C_4H_{10}\)
- Separation factor gradually increases as 3rd or 4th components are introduced
IAST prediction for multicomponent mixture

- Existing literature unary isotherms of C₁-C₄ in MFI are fitted and used for IAST predictions
- Loading of weakly absorbing components is significantly suppressed in quaternary mixture conditions
- Trends observed in IAST simulation are consistent with the experimental results
- **Adsorption dominates the separation mechanism**
Key conclusions and ongoing work

A new fabrication process for thin, 2D MFI-based hollow fiber membranes has been developed

- Dense and uniform 2D MFI nanosheet coating on alumina hollow fibers by vacuum filtration
- Fluoride-media secondary growth yields highly $b$-oriented high flux membranes
- Tertiary TEAOH silica sol growth improved selectivity with minimal reduction in the permeance
- Excellent fluxes and high separation performance for both molecular sieving and adsorption-controlled separation of hydrocarbon mixtures
- Currently developing detailed multicomponent Maxwell-Stefan modeling approach to predict quaternary separation in a wide range of conditions (compositions, sweep/no sweep, temperatures)