Preparation and Application of Ceramic-supported Metal-Organic Framework Membranes

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Outline

- **Background** (MOFs and MOF membranes)
- **Introduction** (my works about MOF membranes)
- **Main**
  - Inner MOF membranes by circulation convection method
  - Micropatterned UiO-66 membranes
- **Conclusion**
Metal-organic frameworks (MOFs)

Metal–organic frameworks (MOFs) are hybrid inorganic–organic materials consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures.

Ref.

Background

❖ Prospection

- Excellent candidates for applications in membrane separation fields.
- Publications and Citations (pure MOF membranes)

**TOPIC:** (metal-organic framework or ZIF) AND (membrane) AND (separation)

**Data:** Web of science
Introduction

What can we do?

Ceramic supports

- Mechanical strength (over 10 N)
- Chemical stability (acid & alkali)
- Thermal stability (over 1000 °C)

MOF crystal examples

Porous supports

- high flux and high selectivity
Introduction

What I have done:

- **Disc**
- **Tube** (e.g., Hollow Fibre)
Introduction

What I have done:

Disc: flat, smooth...

1. Verifying reactive seeding method for metal-carboxylate MOF
   - **Novelty:** High-energy Ball-milling Method for Seeding
   - **Application:** Enantioseparation of racemic diols (2-methyl-2,4-pentanediol)
   - **Target:** Verification of reactive seeding method for metal-carboxylate MOF
   - **Application:** H2 recovery

2. CERAMIC SUPPORTS
   - **Target:** [Zn2(camo)2dabco] (Zn-CD) membrane on porous ZnO support
   - **Application:**
Introduction

What I have done:

**Disc:**
- Fabrication of homochiral MOF membrane for enantioseparation of racemic diols
- Preparation of novel metal-carboxylate system MOF membrane for gas separation

**Hollow Fibre:** Higher membrane area to volume ratio

1. **Novelty:** Hydrophobic MOF membranes on hollow fiber
   **Application:** Recovery of ethanol from ethanol/water mixture
   *Hydrophobic ZIF-71 Membrane Fabricated by Contra-Diffusion*

2. **Novelty:** Inner MOF membranes
   **Application:** H₂ recovery
   Propylene/propane

CERAMIC SUPPORTS

**Fabrication of**
- homochiral MOF membrane for enantioseparation of racemic diols
- Preparation of novel metal-carboxylate system MOF membrane for gas separation

**Application:**
- H₂ recovery
- Propylene/propane
Introduction

What I have done:

Disc:
- Fabrication of homochiral MOF membrane for enantioseparation of racemic diols
- Preparation of novel metal-carboxylate system MOF membrane for gas separation

Hollow Fibre:
- Hydrophobic ZIF-71 Membrane Fabricated by Contra-Diffusion
- ZIF-8 membrane on the inner-surface of ceramic hollow fiber via cycling precursors
  K Huang, WQ Jin, et al., Chem Commun., 2013, 49, 10326
- High C3H6 Selective MOF Membranes in Confined Spaces via Convective Circulation
  K Huang, K Li, et al., Adv. Mater. Interfaces, 2018, 1800287

Designed Special Configuration:

Novelty:
Miniaturization of MOF membranes by patterning the membrane surface

Application:
A lab-on-a-chip device

Micropatterned MOF Membranes
Introduction

What I have done:

Disc: ➢ Fabrication of homochiral MOF membrane for enantioseparation of racemic diols

➢ Preparation of novel metal-carboxylate system MOF membrane for gas separation

Hollow Fibre:

➢ Hydrophobic ZIF-71 membrane fabricated by contra-diffusion

➢ ZIF-8 membrane on the inner-surface of ceramic hollow fiber via cycling precursors
K Huang, WQ Jin, et al., Chem Commun., 2013, 49, 10326

➢ High C\textsubscript{3}H\textsubscript{6} selective MOF membranes in confined spaces via convective circulation
K Huang, K Li, et al., Adv. Mater. Interfaces, 2018, 1800287

Designed Special Configuration:

➢ Micropatterned MOF membranes with enhanced molecular sieving property
Inner MOF membranes

- **Motivation**
  - (Prepare MOF membranes on disc substrates or exterior surface of tubes)
  - MOF membranes are easily damaged during preparation, storage and module assembly.

- **Available way:**
  - Prepare MOF membranes on the inner surface of tubular supports (e.g., hollow fiber)

- **Current method:**
  - (How to offer enough reactants for growth of MOF membranes)
  - Interfacial microfluidic processing driven by syringe pump
  - Cycling precursor driven by peristaltic pump

- **Disadvantages:**
  - Pulsed flow (peristaltic pumps)
  - Volume limit (syringe pumps)
  - Corrosion to the sealing parts
  - Effect of high temperature

Alternative approaches are significant for the development of MOF membranes.
Research Plan

- Domestic heating systems

  Hot water around the house by using only convective action.

  Pump-free MOF synthesis system.

  Convective circulation method

Pump-free Gravity Hot Water systems
Research Plan

- Convective circulation

Schematic of convective circulation synthesis loop:
- Warm colours (Red): higher temperatures
- Cold colours (Blue): lower temperatures

Convective circulation synthesising setup was built using stainless steel tubings.
Substrates: YSZ hollow fiber

(a) YSZ hollow fibre and
(b) 7-bore micro-monolith substrates.

The mean flow pore size is ~90 nm.
N₂ permeance is $1.17 \times 10^{-5} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ (295 K, 1 bar)

- Enhance the membrane area to volume ratio in assembled modules;
- Reduce the capital and operational costs for separation plants.
Preparation of inner MOF membrane

**Ni-LAB**

Synthesis Temp.: \textbf{150 °C}

[\text{Ni}_2(\text{l-asp})_2(\text{bpy})]

\text{bipy: 4,4'-bipyridine}
\text{l-asp: L-aspartic acid}

Ref.
Angew Chem Int Ed. 2006;118:6645–6649.

**ZIF-67**

Synthesis Temp.: \textbf{25-120 °C}

Ref.
J. Am. Chem. Soc. 137, 38, 12304-12311
Chem. Commun., 2016, 52, 12578-12581

**ZIF-8**

Synthesis Temp.: \textbf{25-100 °C}

Ref.
J. Am. Chem. Soc. 2009, 131, 16000–16001
Preparation of inner MOF membrane

**Ni-LAB**

**ZIF-67**

**ZIF-8**

Support: YSZ ceramic substrates
ZIF-8 membrane characterizations

Surface SEM image

Cross-sectional SEM & EDX images

No obvious penetration

YSZ hollow fiber support

XRD

Simulated ZIF-8 pattern

2θ / °

Intensity / a.u.

YSZ

ZIF-8 membrane

ZIF-8 crystals

FTIR

Inner ZIF-8 membrane

ZIF-8 crystals

Transmittance

Wavenumber (cm⁻¹)

3000 2500 2000 1500 1000
ZIF-8 membrane separation performance

(a) Pure gas permeances and (b) ideal selectivities of H$_2$ over other gases for the five samples (M1-M5), confirming the consistency of membrane quality. The data were achieved through the constant-volume/variable-pressure setup.

◆ Five ZIF-8 membranes were synthesized and showed very consistent performances when tested with five different gases.

◆ The gas permeances followed the sequence of H$_2$ > CO$_2$ > N$_2$ > CH$_4$ > C$_3$H$_6$, and showing good ideal selectivities for hydrogen recovery.
Binary gas separation test of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixture

Outstanding propylene/propane mixture gas separation factor with the maximum valve, about 140, by testing over 120 hours.

ZIF-8 membrane separation performance

- 7-bore YSZ micro-monolith supported inner ZIF-8 membrane

A good propylene/propane separation factor, around 30.

Micropatterned MOF Membranes

Motivation?

- Laboratory scale
- Scale-up (industry)

Available way:
- Incorporating MOF membranes into devices or instruments
- As a key role in a lab-on-a-chip device through miniaturization

Target:
- To demonstrate the feasibility of miniaturization of MOF membranes by patterning the membrane surface
Preparation of Micropatterned MOF Membranes

- Bottom-up method to prepare Micropatterned MOF membranes

Schematic diagram of patterned YSZ ceramic substrates and UiO-66 membranes prepared

- ① Casting
- ② Phase-inversion
- ③ Sintering
- ④ In-situ growth

Array of cuboids
Length: ~75 um
Width: ~75 um
Height: ~32 um

PDMS: polydimethylsiloxane
YSZ: yttria-stabilized zirconia (YSZ)

Characterization

Surface SEM images

Cross-section SEM images

~900 nm (top parts)

~300 nm (valley parts)
Characterization

◆ Different features of the patterns

Channeled patterns

Cylindrical patterns
Micropatterned MOF Membranes

**Membrane thickness**

- only less than 250 nm (at the valleys)
- ~1.0 μm (at the top of the cylinders)

*Example: Cylindrical UiO-66 membranes:*

- only less than 250 nm (at the valleys)
- ~1.0 μm (at the top of the cylinders)

Such a trend can be attributed to the concentration profile of reactants over the patterned surface during the in-situ hydrothermal synthesis process.
Micropatterned MOF Membranes

Membrane thickness

SEM images of two channeled UiO-66 membranes with different depth:
(a, b) 10 μm;
(c, d) 50 μm.
Micropatterned MOF Membranes

- Separation performance of UiO-66 membranes with different patterns.

- Organic solvent dehydration:
  - 10 wt.% water/n-butanol
    - above 99 wt.% in the permeate
    - separation factor of over 1,000

- Equal quality with the unpatterned membrane
- Considerably higher flux than the unpatterned membrane
Conclusions

Ceramic supports
- Disc
- Hollow Fibre
- Micropatterned

MOF materials
- [Ni$_2$(L-asp)$_2$(bipy)] (Ni-LAB)
- [Zn$_2$(cam)$_2$dabco] (Zn-CD)
- ZIF-67
- ZIF-8
- ZIF-71
- UiO-66

Applications
- Chiral separation
- Gas separation
  - H$_2$ recovery
  - CO$_2$ capture
  - C$_3$H$_6$/C$_3$H$_8$
- Bio-ethanol recovery
- Dehydration
  - organic solvent

MOFs are very promising materials for the membrane separation fields
Thanks for Your Attention!