

## **Supporting information**

**Steam-stable hydrophobic ITQ-29 molecular sieve membrane with H<sub>2</sub> selectivity prepared by secondary growth using Kryptofix 222 as SDA**

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## Experimental methods

### 1. Materials

Chemicals were used as received: Tetraethyl orthosilicate (TEOS, >98%, Merck); germanium dioxide (99.99%, Aldrich); tetramethylammonium hydroxide (TMAOH, 25 % in water, Abcr); 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Kryptofix 222, hereafter K222, 98%, Acros); hydrofluoric acid (48 % in water, Merck); doubly distilled water. Porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disks (Inocermic GmbH, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 100 nm particles in the top layer) were used as supports.

### 2. Synthesis of ITQ-29 seeds

For the synthesis of the ITQ-29 seeds, the gel with the molar ratio of 0.67TEOS : 0.33GeO<sub>2</sub> : 0.25K222 : 0.25TMAOH : 0.5HF : 30H<sub>2</sub>O, was prepared according to the procedure reported elsewhere.<sup>1</sup> The gel was prepared by dissolving TEOS in an aqueous solution of K222 and TMAOH, and then the appropriate amount of GeO<sub>2</sub> was added. The mixture was stirred for 24 h at room temperature until the ethanol formed upon hydrolysis of TEOS and the appropriate excess of water was evaporated to reach the gel composition. Finally, an aqueous solution of hydrofluoric acid was added and within a few seconds the whole mixture became viscous. The final mixture was again stirred for 30 min at room temperature. The synthesis gel was introduced in a Teflon-lined stainless steel autoclave and heated in a microwave oven (Ethos 1, MLS) with a rate of 8 °C min<sup>-1</sup> to 150 °C for 6 h. After cooling, the solids were filtered, washed with 0.1 M HCl solution and distilled water in an ultrasonic cleaner several times, and then dried at 373 K.

### 3. Synthesis of ITQ-29 membrane

The ITQ-29 membranes were prepared by secondary growth method on seeded supports. Before hydrothermal synthesis, the surface of Al<sub>2</sub>O<sub>3</sub> was coated with ITQ-29 seeds by a dipping-evaporation strategy.<sup>2</sup> ITQ-29 seeds prepared above were dispersed by ultrasonic treatment in ethanol-water (50:50) and a 0.5 wt.% seed suspension was obtained. The seed

suspension was given the horizontally oriented supports on a Teflon holder. After water evaporation at room temperature for 20 h, the ITQ-29 seeds formed a homogeneous coat on the support surface. Further heating (at 373 K for 2 h) was helpful to improve the attachment of the seeds to the support surface.

The gel for the synthesis of the ITQ-29 membranes was prepared according to the same procedure as preparation of seeds, but with the molar ratio of 0.67TEOS : 0.33GeO<sub>2</sub> : 0.25K<sub>2</sub>CO<sub>3</sub> : 0.25TMAOH : 0.5HF : 60H<sub>2</sub>O. The support was placed horizontally in the Teflon-lined stainless steel autoclave, and then the synthesis solution was poured into the autoclave. After crystallization times of 3 days at 423 K in an oven with air circulation, the autoclave was cooled down, and the solution was decanted off. The membrane was washed with deionized water, and then dried at 373 K overnight.

#### *4. Characterization of ITQ-29 membrane*

Scanning electron microscopy (SEM) micrographs were taken on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10  $\mu$ A. Phase purity and crystallinity of the ITQ-29 membranes were confirmed by X-ray diffraction (XRD). The chemical composition of the ITQ-29 membrane was characterized by energy-dispersive X-ray spectroscopy (EDXS) using the same SEM microscope at 20 kV and 20  $\mu$ A. The X-ray diffraction (XRD) patterns were recorded at room temperature under ambient conditions with a PANalytical instrument (X'Pert-MPD, Cu K $\alpha$  with  $\lambda$  = 1.5418 Å) at 40 kV and 50 mA.

#### *5. Separation properties of ITQ-29 membrane*

Before gas permeation, the as-synthesized ITQ-29 membrane was sealed and in-situ on-stream activated at 300 °C by using single gas O<sub>2</sub> in the Wicke-Kallenbach permeation apparatus (Fig. S6). After activation, the feed gases were fed to the side of the membrane, and sweep gas was fed on the permeate side to keep the concentration of permeating gas low providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. For both single and mixture gas permeation, the fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromatograph (HP6890) was used to measure the gas concentrations, as shown in Fig. S6. The separation factor  $\alpha_{i,j}$  of a

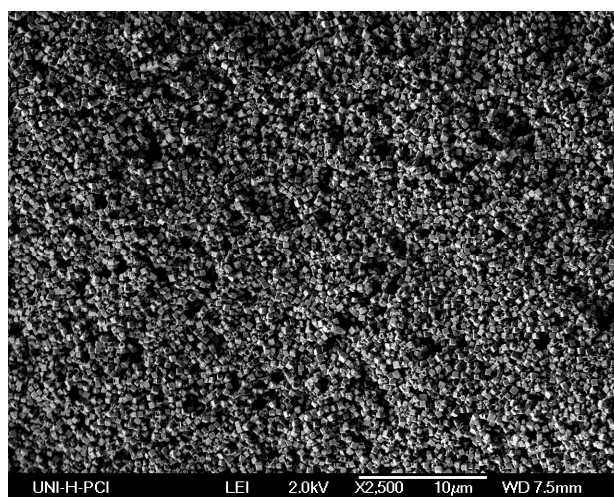
binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the retentate, as show in Eq. 1.

$$\alpha_{i/j} = \frac{y_{i,Perm} / y_{j,Perm}}{y_{i,Ret} / y_{j,Ret}} \quad (1)$$

## Reference

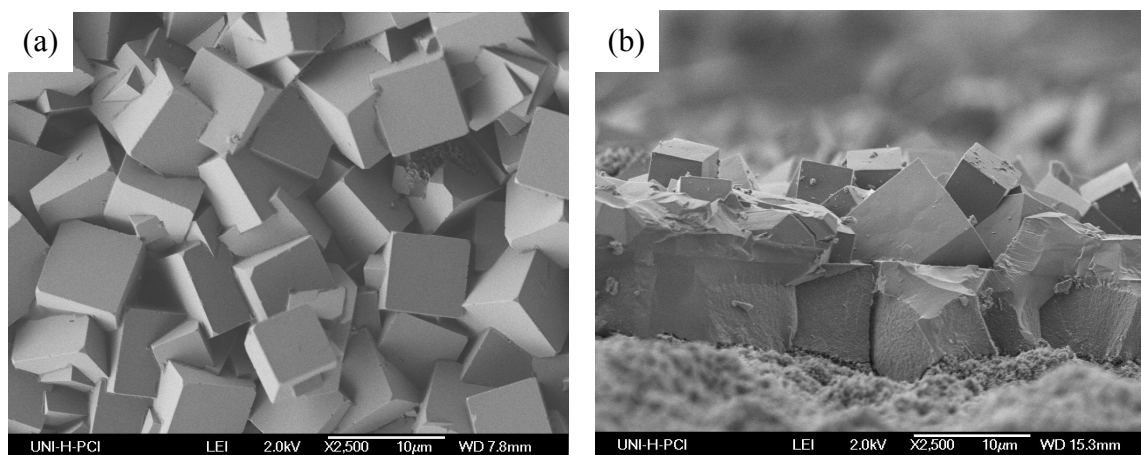
- [1] A. Huang and J. Caro, *Micropor. Mesopor. Mater.*, 2010, 129, 90.
- [2] A. Huang, F. Liang, F. Steinbach, T. M. Gesing and J. Caro, *J. Am. Chem. Soc.*, 2010, 132, 2140.

**Fig. S1** SEM images of ITQ-29 seeds layer on  $\text{Al}_2\text{O}_3$  support surface.



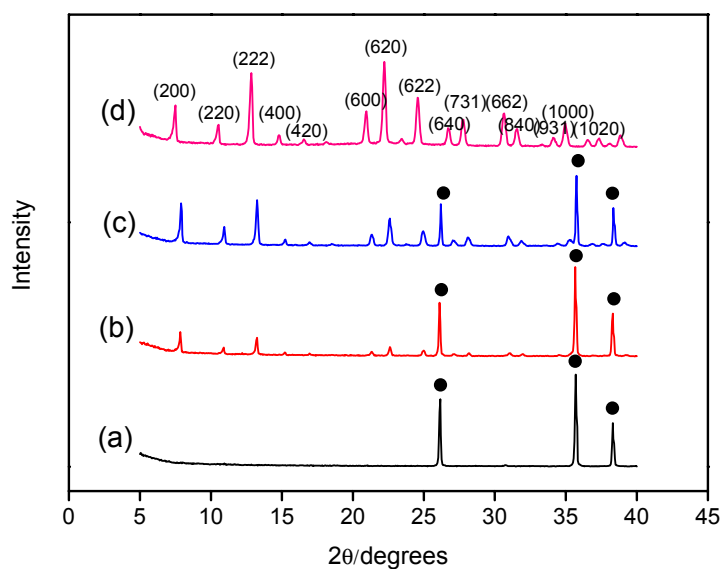
**Figure S1**

**Fig. S2** SEM images of (a) surface view and (b) cross-section of the ITQ-29 membrane prepared without seeding.



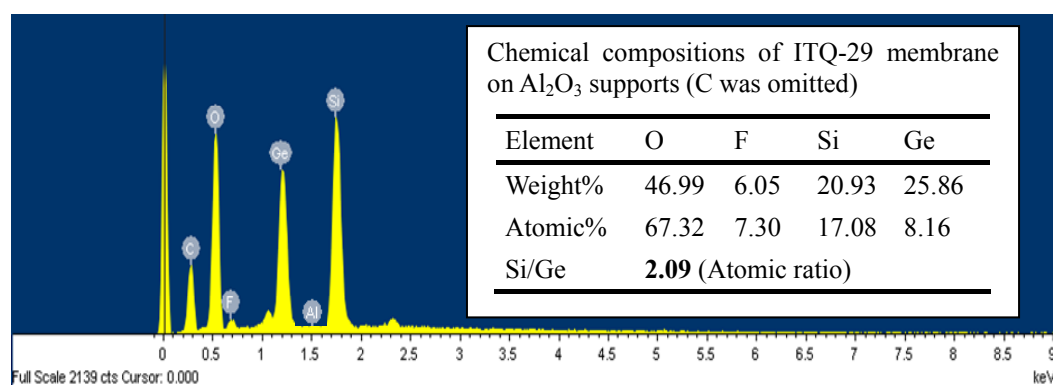
**Figure S2**

**Fig. S3.** XRD patterns of the (a) bare  $\text{Al}_2\text{O}_3$  support, (b) seeded  $\text{Al}_2\text{O}_3$  support, (c)  $\text{Al}_2\text{O}_3$ -supported ITQ-29 membrane and (d) ITQ-29 powder. (•):  $\text{Al}_2\text{O}_3$  support, (not marked): ITQ-29 crystals.



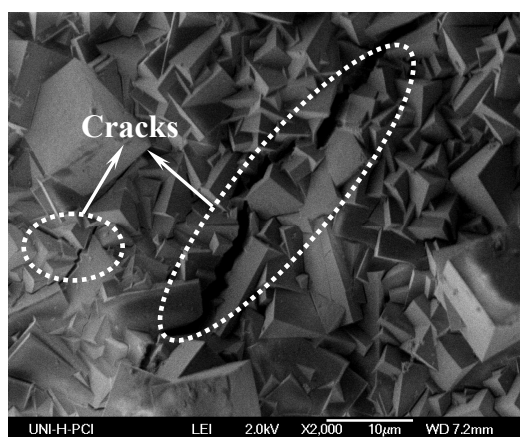
**Figure S3**

**Fig. S4.** EDXS pattern and chemical composition of the Al<sub>2</sub>O<sub>3</sub>-supported ITQ-29 membrane prepared with seeding method.



**Figure S4**

**Fig. S5** SEM images of activated ITQ-29 membrane treated in air oven at 300 °C.



**Figure S5**

**Fig. S6.** Measurement equipment for both single and mixed gas permeation.

*Legend:*

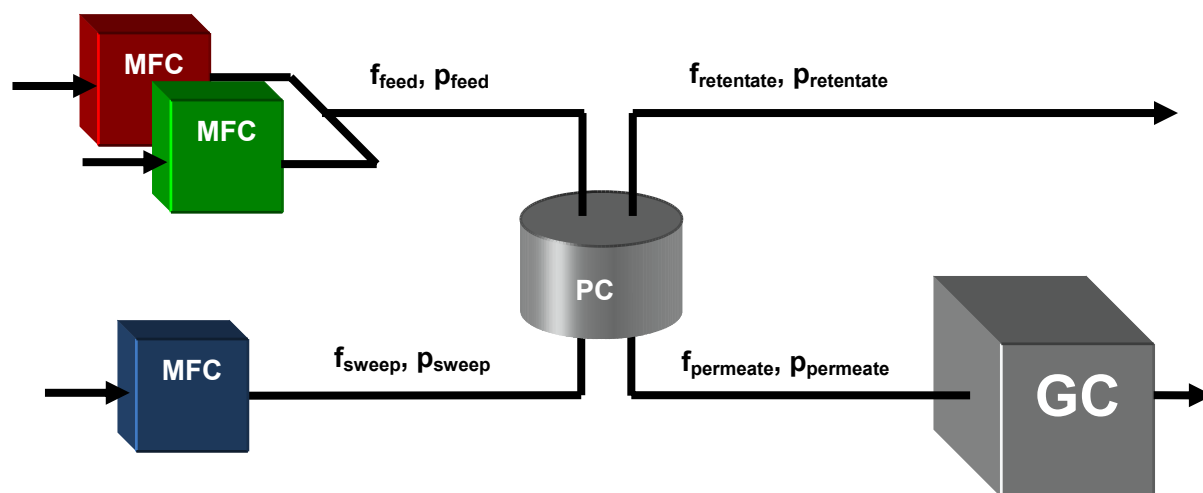
**MFC:** mass flow controller

**PC:** permeation cell with mounted membrane

**GC:** gas chromatograph

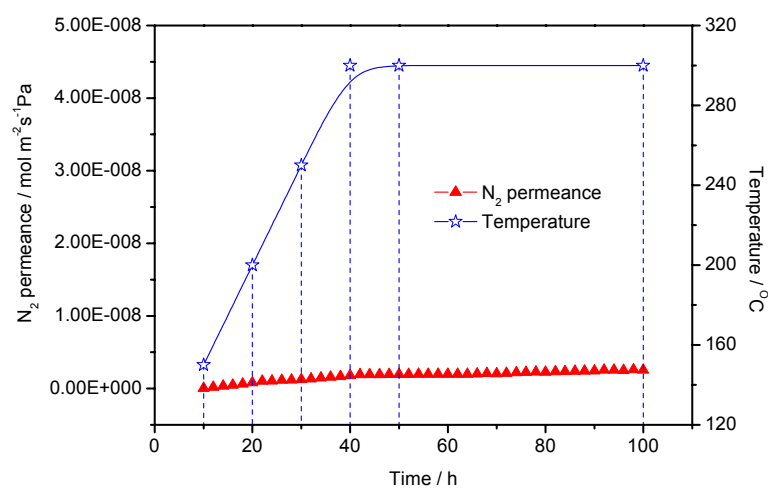
**f:** volumetric flow rate

**p:** pressure



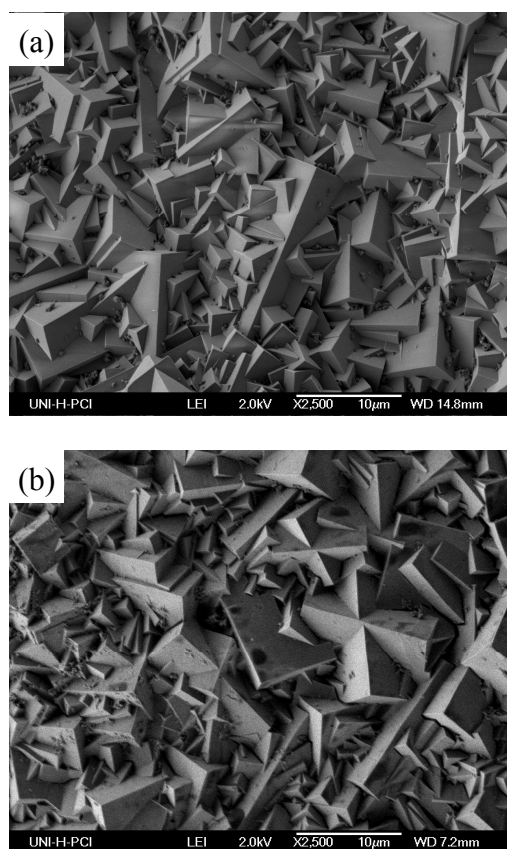
**Figure S6**

**Fig. S7.** Variation of N<sub>2</sub> permeance from single gas N<sub>2</sub> through the ITQ-29 membrane during the in-situ on-stream activation.



**Figure S7**

**Fig. S8** SEM images of (a) as-synthesized ITQ-29 membrane (b) activated ITQ-29 membrane treated in O<sub>2</sub> at 300 °C with in-situ on-stream activation strategy.



**Figure S8**

**Table S1** Single and mixture gases permeances ( $\text{mol}/\text{m}^2\text{s}^1\text{Pa}^1$ ) and separation factors for the ITQ-29 membrane at 300 °C and 1 bar with 1:1 binary mixtures of  $\text{H}_2$  and  $\text{C}_3\text{H}_8$ .

**Table S1**

| $\text{Gas}_{i/j}$                | Knudsen constant | Performances of the ITQ-29 membrane                                         |                                                                             |                            |                                                                             |                                                                             |                      |
|-----------------------------------|------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------|
|                                   |                  | Single gas                                                                  |                                                                             |                            | Mixed gases                                                                 |                                                                             |                      |
|                                   |                  | Permeances(i)<br>( $\text{mol}/\text{m}^2\cdot\text{S}^1\cdot\text{Pa}^1$ ) | Permeances(j)<br>( $\text{mol}/\text{m}^2\cdot\text{S}^1\cdot\text{Pa}^1$ ) | Ideal Separation<br>factor | Permeances(i)<br>( $\text{mol}/\text{m}^2\cdot\text{S}^1\cdot\text{Pa}^1$ ) | Permeances(j)<br>( $\text{mol}/\text{m}^2\cdot\text{S}^1\cdot\text{Pa}^1$ ) | Separation<br>factor |
| $\text{H}_2/\text{CO}_2$          | 4.7              | $4.18 \times 10^{-7}$                                                       | $5.37 \times 10^{-8}$                                                       | 7.8                        | /                                                                           | /                                                                           | /                    |
| $\text{H}_2/\text{N}_2$           | 3.7              | $4.18 \times 10^{-7}$                                                       | $6.17 \times 10^{-8}$                                                       | 6.8                        | /                                                                           | /                                                                           | /                    |
| $\text{H}_2/\text{CH}_4$          | 2.8              | $4.18 \times 10^{-7}$                                                       | $6.79 \times 10^{-8}$                                                       | 6.2                        | /                                                                           | /                                                                           | /                    |
| $\text{H}_2/\text{C}_3\text{H}_8$ | 4.7              | $4.18 \times 10^{-7}$                                                       | $2.88 \times 10^{-9}$                                                       | 145.1                      | $3.64 \times 10^{-7}$                                                       | $2.86 \times 10^{-9}$                                                       | 127.1                |