

# Development of Innovative Gas Separation Membranes through Sub-Nanoscale Materials Control — Inorganic CO<sub>2</sub> separation membranes —

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## 2. Objective:

Carbon dioxide capture and storage (CCS) could allow the utilization of abundant fossil fuel reserves, while significantly decreasing emissions of CO<sub>2</sub> to the atmosphere. However, the cost of CCS, especially of CO<sub>2</sub> capture, is still too expensive to consider as a cost effective technique. This project intends to develop a variety of efficient, low-cost polymeric and inorganic CO<sub>2</sub> separation membranes that will be a game changing technology. Material structure engineering at the scale of gas molecules will be used to increase the permeability and selectivity of the membrane. As for the inorganic materials, zeolite and functionalized mesoporous membranes have been prepared. The preparation of ultra-thin, defect-free membranes will be investigated.

## 3. Background:

The process of membrane separation of CO<sub>2</sub> from other gases is an active field, but the best membrane today is still considered too energy intensive and expensive to be implemented on a large scale. Gas separation in membranes is driven by providing a pressure difference across the membrane. In order to obtain a sufficiently pure stream of CO<sub>2</sub>, the selectivity for CO<sub>2</sub> must be high. In addition, to attain the compact membrane facility, a high permeability is also required. Many current systems require a large membrane area and cascading in order for the gas to permeate through multiple membrane stages to achieve the desired flow rate and purity. As such, new membrane types are required to have high permeability and selectivity, as well as long-term durability. Two areas of gas separation membrane research are currently focused on the development of polymeric and inorganic membranes. Polymeric membranes are relatively easy to manufacture and are well-suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. In addition, by carbonizing these polymeric materials it is possible to obtain a molecular sieve capability. Inorganic membranes on the other hand, have much greater thermal and chemical stability. Inorganic materials including zeolites and silicas have appropriately-sized pores that can act as molecular sieves to separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play a role in separating gas molecules. Since the effective sizes of CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and other gases present in fossil fuel conversion systems are very similar, the membrane pore spaces must be controlled on a scale comparable to the size differences among these gas molecules. This will be achieved for a variety of membrane types using several different techniques. In this paper, we describe the development of new membrane types with well-controlled sub-nanostructures prepared from inorganic materials: functionalized mesoporous oxide membranes and molecular sieving zeolite membranes.

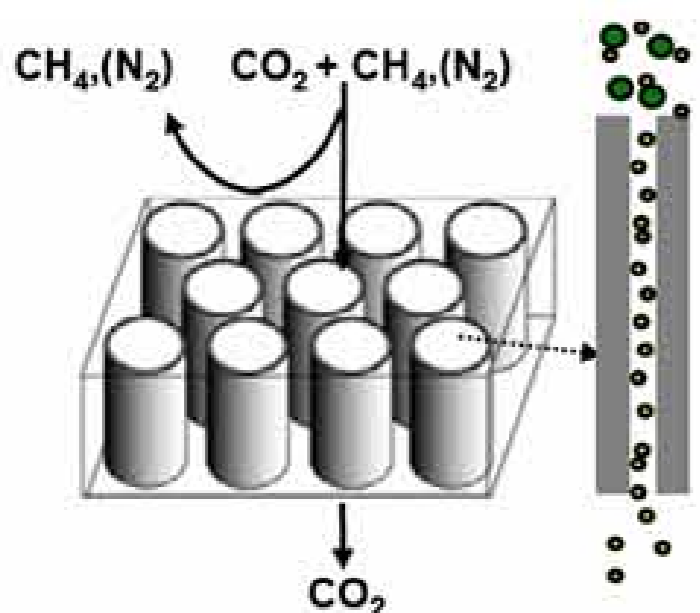


Figure 1: Porous inorganic membranes act as molecular sieves, differentiating gas molecules by effective size.

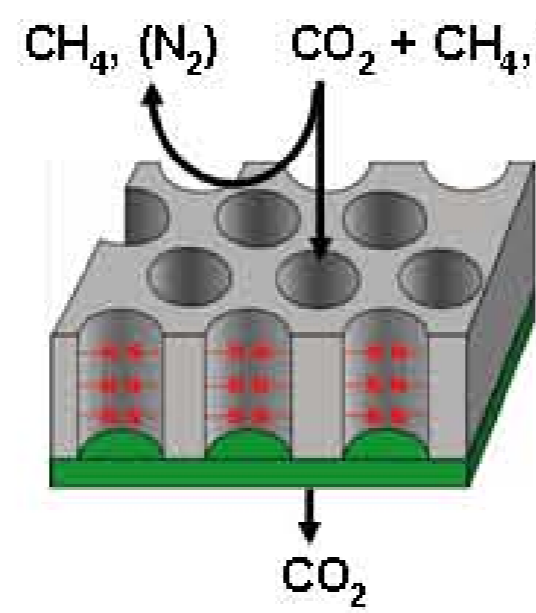


Figure 2: Inner surface of functionalized mesoporous oxide membrane which is effective for CO<sub>2</sub> adsorption.

## 4. Approach:

### 4.1. Development of Functionalized mesoporous oxide membrane

The amine modification of the pore walls of mesoporous silicas is effective for selective CO<sub>2</sub> adsorption. In this study, various functionalized mesoporous silica membranes for CO<sub>2</sub> separation were successfully prepared on porous alumina supports by hydrothermal treatment and spin-coating of silica sol.

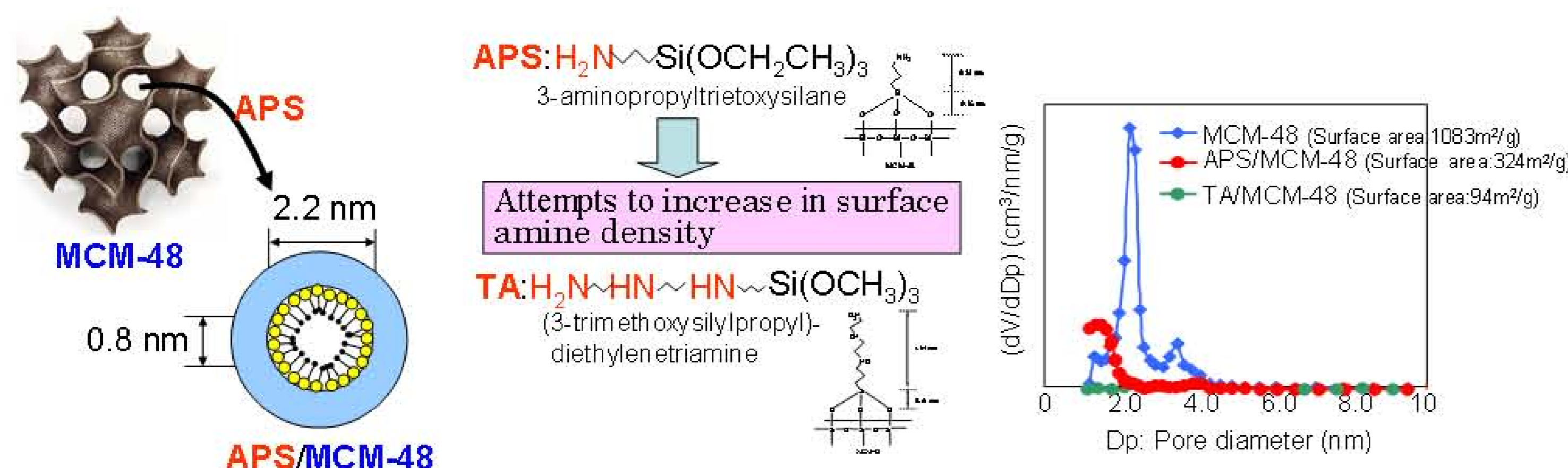


Figure 3: Schematic illustration and pore distribution of amine-modified MCM-48.

### 4.2. Development of zeolite membrane

#### 4.2.1. Challenging development of zeolite membrane without defects

We have demonstrated the novel synthesis of a defect-free zeolite membrane suitable for CO<sub>2</sub> separation. Here, the porous substrate has been filled with zeolite crystals. Figure 4 shows a scheme illustrating the 'melt-filling method'. We found that the chemical and physical conditions must be optimized for the melting, plasticization, and re-crystallization of the zeolite membrane.

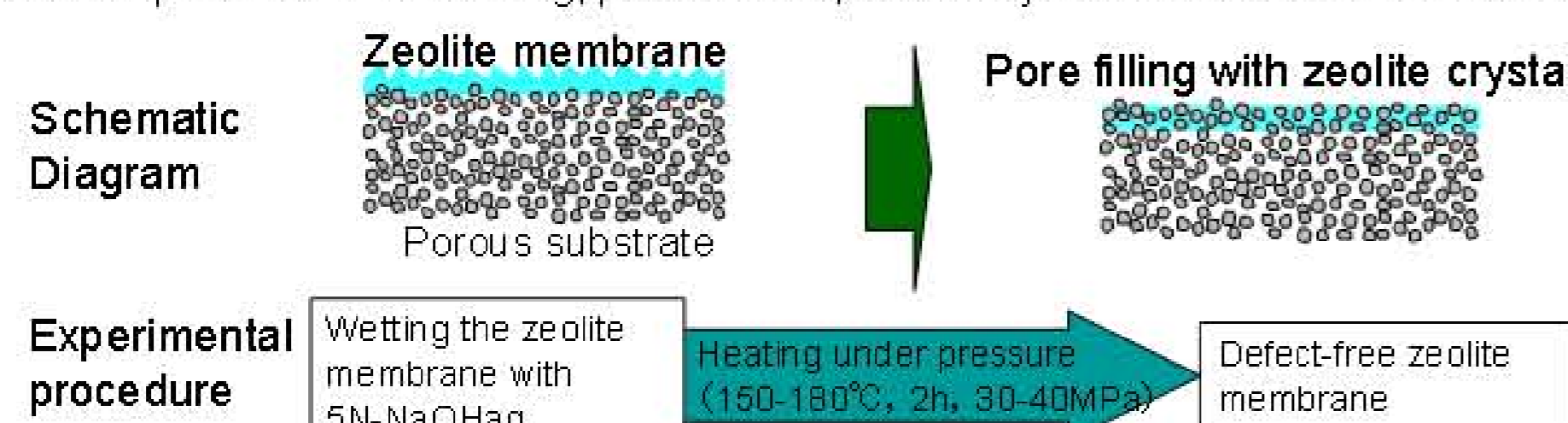


Figure 4: Schematic illustration of the melt-filling method involving the melting and re-crystallization of the zeolite membrane.

#### 4.2.2. Searching for a suitable zeolite topology

In collaboration with the University of Tokyo, we have been undertaking a simulation forecast of the optimum pore structure for CO<sub>2</sub> separation, and investigating the synthesis method of a new type of porous materials effective for CO<sub>2</sub> separation. We decided to adopt the Dynamic Monte Carlo (DMC) that calculates the transport diffusivities for gas mixtures in various zeolite structures. Based on the simulation results, we have selected a number of candidate zeolite structures for use in CO<sub>2</sub> separation studies. CO<sub>2</sub> adsorption capacity of hydrophilic zeolite is lost completely by coexistent water, so pure silica or high silica type zeolite should be used for CO<sub>2</sub> separation processes in high moisture conditions, such as stack gas. Therefore, on top of that, we have chosen several pure or high silica type zeolite.

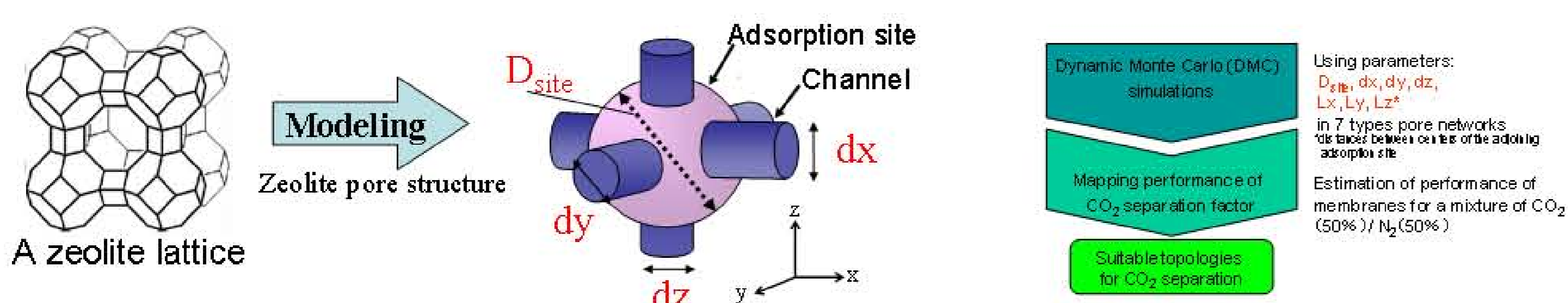


Figure 5: Searching for a suitable zeolite topology. Ref.: H.Takaba et al, ZMPC2006, OC101, (2006).

## 5. Major Results:

### 5.1. Development of Functionalized mesoporous oxide membrane

Mesoporous silica membranes were prepared on porous alumina supports by hydrothermal and spin-coating method. Both of the amine-modified membranes showed high CO<sub>2</sub> permeability (300~800). Amine efficiency for CO<sub>2</sub> capture was improved by increase in surface density of amine. However APS-Modification of MCM-48 membrane is more effective than TA-modification for the CO<sub>2</sub> separation performance. Molecular size of TA is too large for the modification of the pore wall of MCM-48.

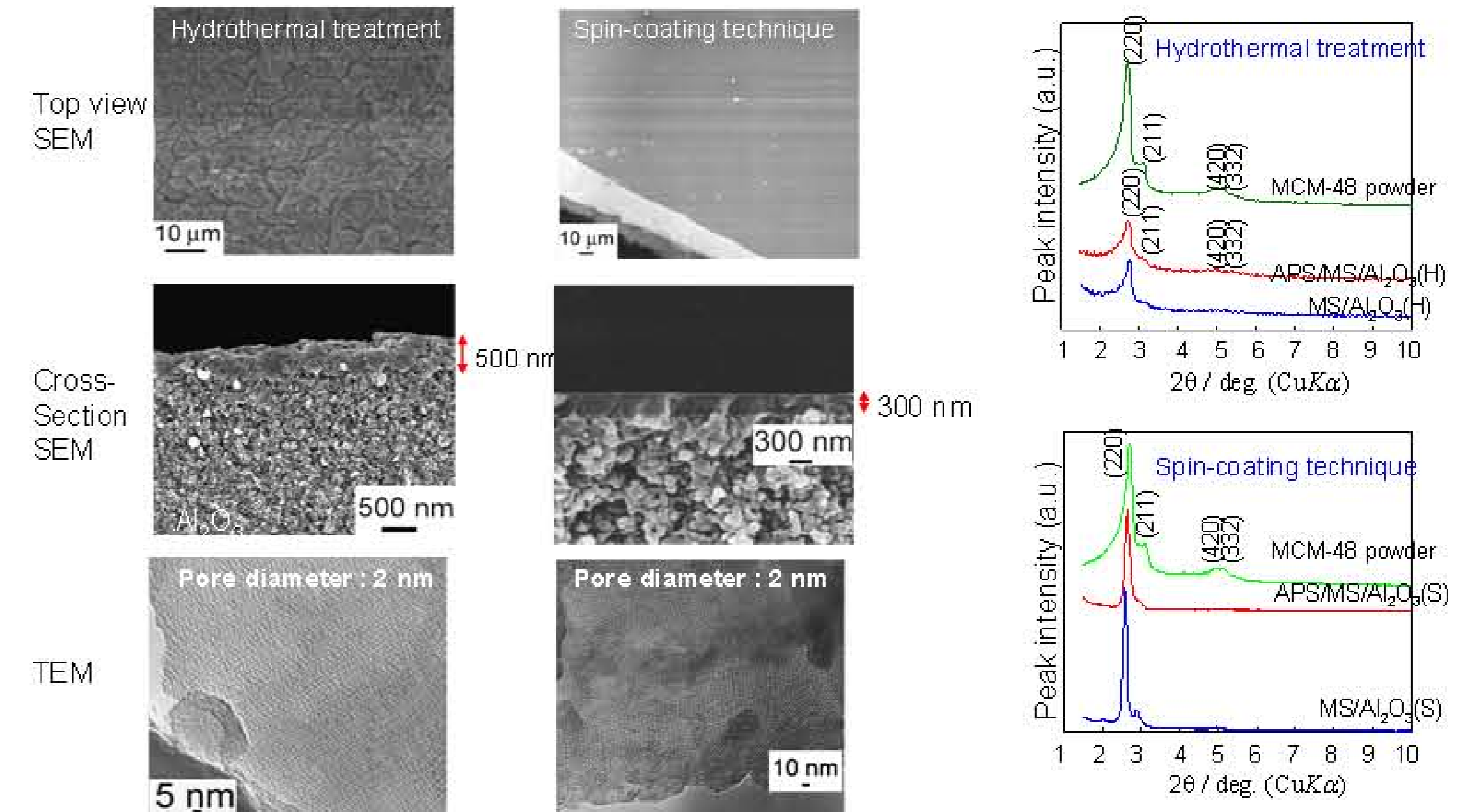


Figure 6: SEM and TEM images, and XRD patterns of MCM-48 membrane synthesized by hydrothermal treatment and spin coating technique.

Table 1: CO<sub>2</sub> separation properties of Modified MCM-48 membrane.

Substrate	Temp (K)	Permeance [mol·sec <sup>-1</sup> ·m <sup>-2</sup> ·Pa]		CO <sub>2</sub> /N <sub>2</sub> selectivity
		CO <sub>2</sub>	N <sub>2</sub>	
Al <sub>2</sub> O <sub>3</sub> substrate	298	1.1 × 10 <sup>-4</sup>	1.1 × 10 <sup>-4</sup>	1.0 <sup>1)</sup>
MS/Al <sub>2</sub> O <sub>3</sub> (H)	298	1.0 × 10 <sup>-7</sup>	1.4 × 10 <sup>-7</sup>	0.8 <sup>1)</sup>
MS/Al <sub>2</sub> O <sub>3</sub> (S)	298	3.4 × 10 <sup>-8</sup>	4.1 × 10 <sup>-8</sup>	0.8 <sup>1)</sup>
APS/MS/Al <sub>2</sub> O <sub>3</sub> (H)	333	6.1 × 10 <sup>-8</sup>	8.5 × 10 <sup>-11</sup>	72 <sup>1)</sup>
APS/MS/Al <sub>2</sub> O <sub>3</sub> (H)	373	6.1 × 10 <sup>-8</sup>	1.8 × 10 <sup>-11</sup>	340 <sup>1)</sup>
APS/MS/Al <sub>2</sub> O <sub>3</sub> (S)	373	1.0 × 10 <sup>-8</sup>	1.2 × 10 <sup>-11</sup>	800 <sup>1)</sup>
TA/MS/Al <sub>2</sub> O <sub>3</sub> (H)	333	6.9 × 10 <sup>-8</sup>	2.3 × 10 <sup>-11</sup>	300 <sup>1)</sup>
TA/MS/Al <sub>2</sub> O <sub>3</sub> (S)	333	2.8 × 10 <sup>-8</sup>	1.4 × 10 <sup>-11</sup>	20 <sup>1)</sup>

Test gas: CO<sub>2</sub>/N<sub>2</sub> = 20/80 1) After 1h, 2) After 24h  
H: Hydrothermal treatment, S: Spin-coating technique

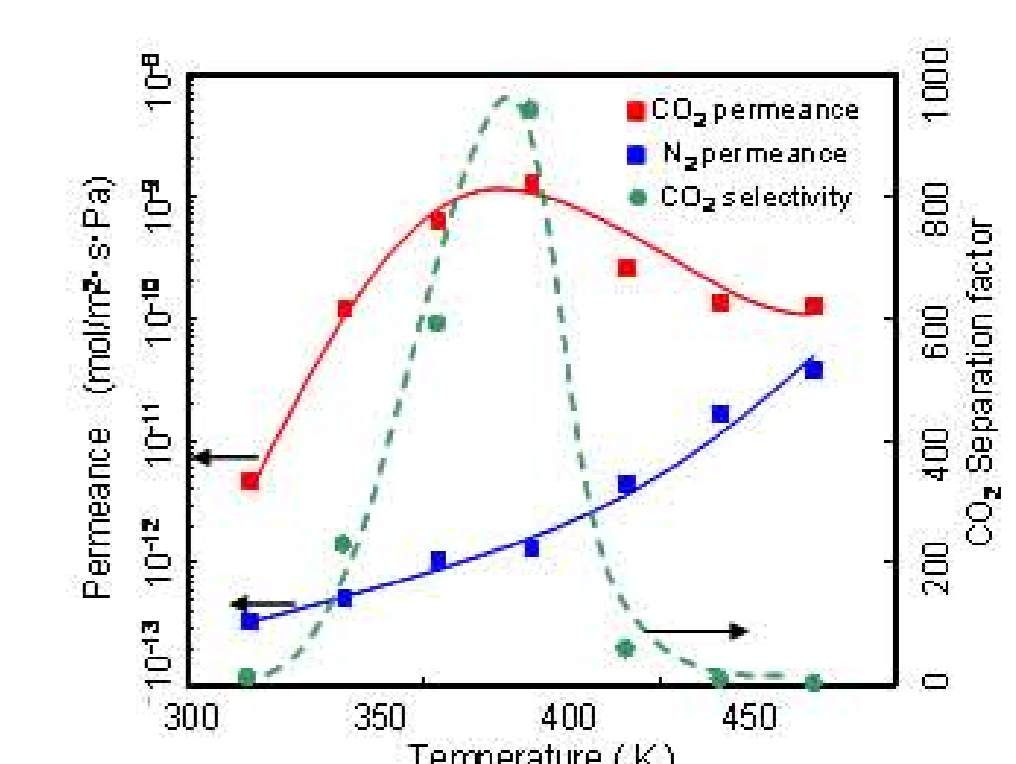


Figure 7: Temperature dependence of gas permeability of APS/MS/Al<sub>2</sub>O<sub>3</sub>(S).

Our Target: High permeability  
Permeance 1000 times  
High selectivity  
α<sub>CO<sub>2</sub>/N<sub>2</sub></sub> = 1000

### 5.2. Development of zeolite membrane

#### 5.2.1. Challenging development of zeolite membrane without defects

From the XRD measurement, it was revealed that these composites had the same diffraction pattern; there was no phase transition and no by-product before and after the Melt-filling synthesis. The gas permeability measurements of the zeolite membrane prepared by the melt-filling method are currently in the process of evaluation. For example, while the CO<sub>2</sub>/N<sub>2</sub> separation selectivity of the zeolite Y membrane was 4, the selectivity became 23 with the melt-filling synthesized membrane. However, the separation selectivity of the membranes formed by this method tends to be low. We assumed that this is due to some defects in the formed zeolite membranes.

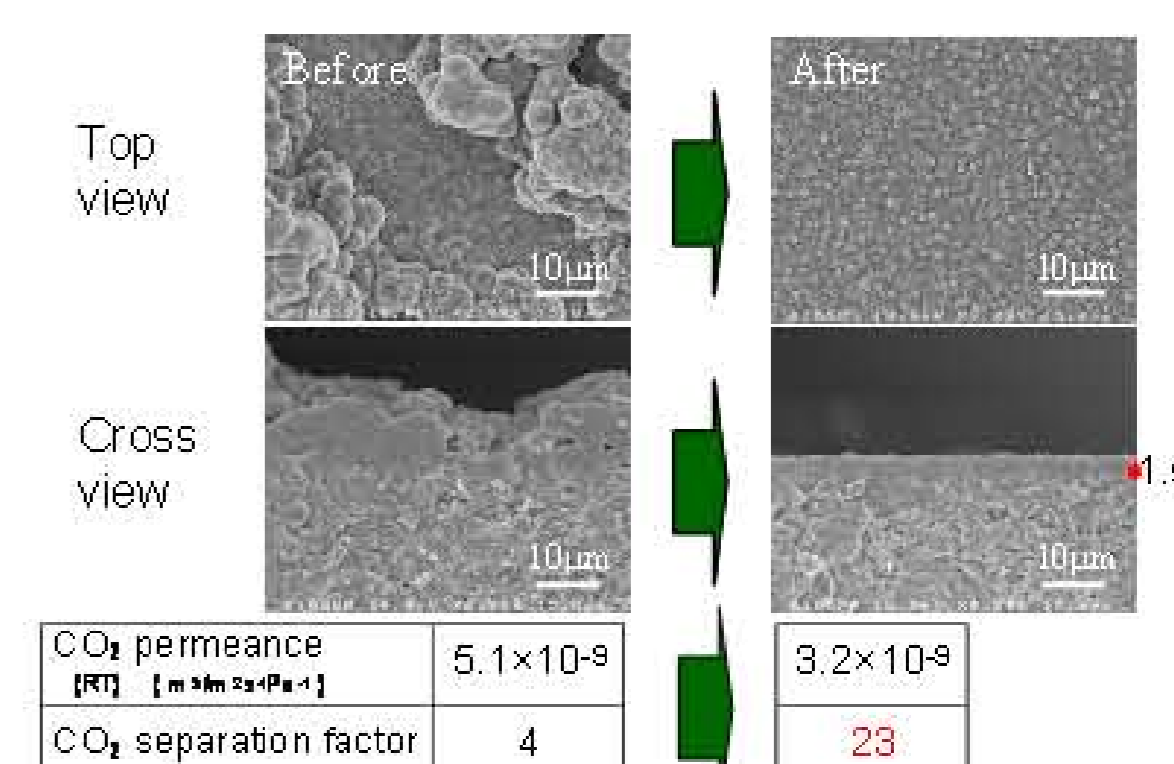


Figure 11: CO<sub>2</sub> separation performance with the melt-filling synthesized membrane.

#### 5.2.2. Searching for a suitable zeolite topology

We found that the effective zeolite membrane has pores that correspond to the seven membered ring (~0.34nm), and it has large adsorption sites and cages that have a lot of channels. Based on the simulation results, we have selected a number of candidate zeolite structures for use in CO<sub>2</sub> separation studies and have begun synthesis of new zeolite membranes. In addition, we are continuing to prepare several zeolite seed crystals, from which several new zeolite membranes are anticipated. The melt-filling method will be adapted to the newly prepared zeolite membranes for improvement of CO<sub>2</sub> separation properties.

Table 2: Prospective candidates according to DMC simulation results.

Framework type	Diameter of channel (nm)	Channel system	Si/Al ratio in typical composition
1.KFI	0.30 × 0.30	3 - dimensional	2.2
2.CHA	0.38 × 0.38	3 - dimensional	2 *preferably higher
3.FER	0.42 × 0.54 × 0.35 × 0.48	2 - dimensional	5
4.RHO	0.36 × 0.36	3 - dimensional	3
5.PAU	0.36 × 0.36	3 - dimensional	3.4

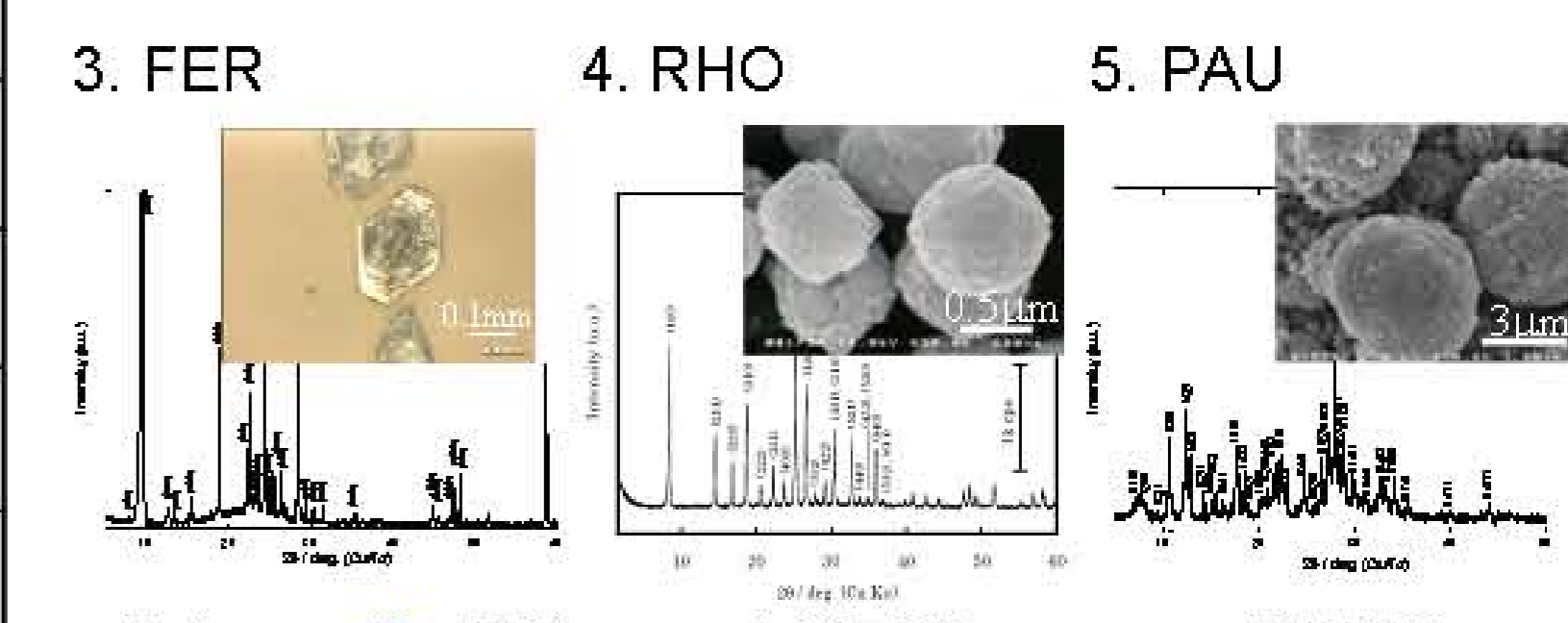


Figure 10: Newly prepared pure silica FER(a), RHO(b), and PAU(c) crystals.

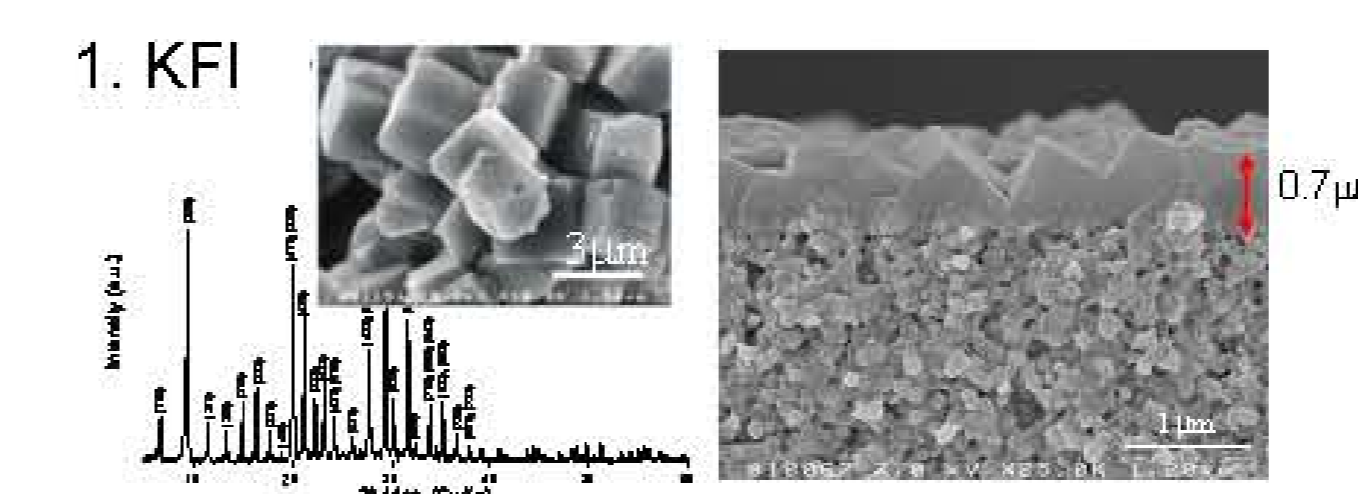


Figure 8: Newly prepared KFI crystal and ultra-thin KFI zeolite membrane.

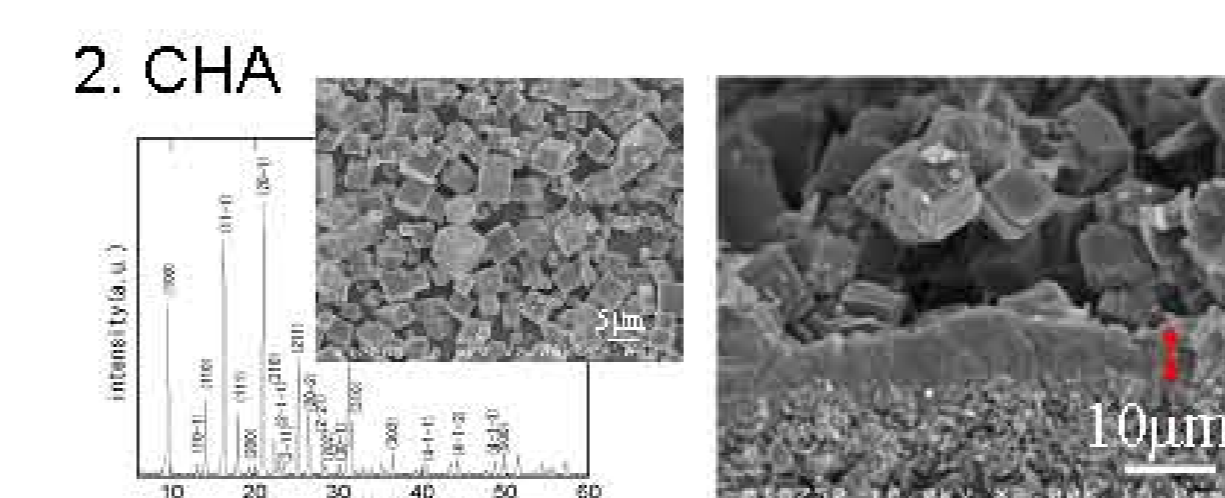


Figure 9: Newly prepared pure silica CHA crystal and zeolite membrane.

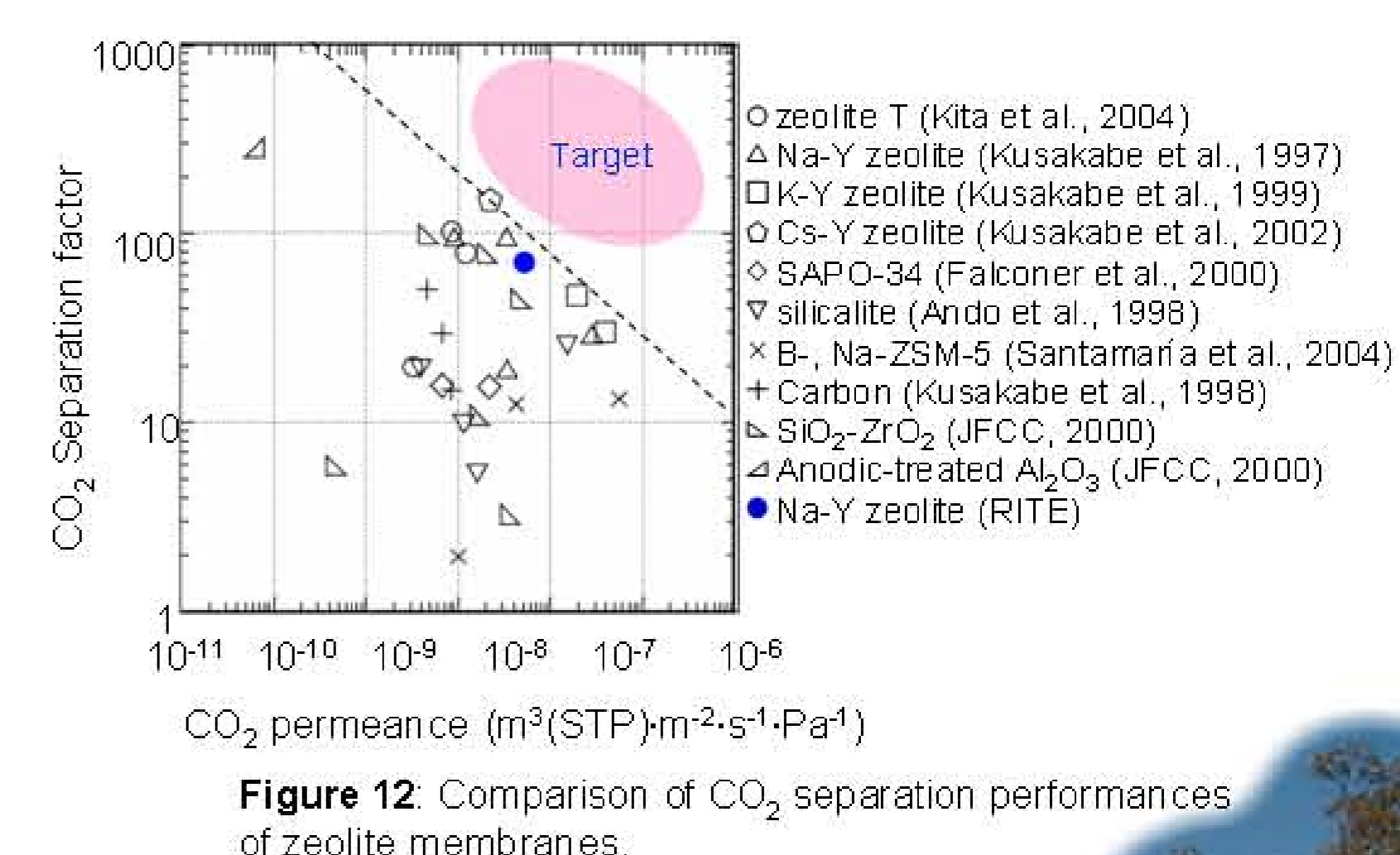


Figure 12: Comparison of CO<sub>2</sub> separation performances of zeolite membranes.