

Chapter III

Experimental

3.1. Membrane preparation

3.1.1. Chemicals

All chemicals in these experiments are listed with grade of purity and manufacturers as shown in Table 3.1.

Table 3.1 Source of chemicals

Chemicals	Grade of purity	Manufacturers
Tetrapropylammonium bromide (TPABr)	98 %	Fluka, Switzerland.
Sodium hydroxide (NaOH)	98 %	J.T. Baker Inc., U.S.A.
Ludox (SiO ₂ colloidal)	40 % w/w	Aldrich Chemical Co., Inc., U.S.A.
Silica fumed (SiO ₂)	Purity	BDH Chemical Ltd., England.
Oxygen gas (O ₂)	High purity	TIG Co., Ltd., Thailand.
Nitrogen gas (N ₂)	High purity	TIG Co., Ltd., Thailand.
Helium gas (He)	High purity	TIG Co., Ltd., Thailand.
Hydrogen gas (H ₂)	High purity	TIG Co., Ltd., Thailand.
Air zero	-	TIG Co., Ltd., Thailand.
o-Xylene	99 %	Fluka, Switzerland.
m-Xylene	99 %	Fluka, Switzerland.
p-Xylene	99 %	Fluka, Switzerland.

3.1.2. Equipment

The main equipment for the experiments are shown in Table 3.2.

Table 3.2 Main equipment

Equipment	Model	Manufacturers
Autoclave	276AC2 T304	Parr Instrument Company, U.S.A.
Furnace	VCTF 4	Vecstar, U.K.
Simultaneous - Thermoanalyzer	STA 409C	Netzsch, German.
Scanning Electron - Microscope	JSM 6400	Jeol, Japan.
X-ray Diffractometer	JDX 8030	Jeol, Japan.
Gas Chromatograph	3800	Varian Chromatography Systems, U.S.A.

3.1.3. Procedures

The membrane was prepared as follows:

3.1.3.1 Support treatment

The borosilicate glass disc supports 1-cm. in diameter with pore sizes 16-40 μm . and 2-cm. diameter with pore sizes 4-5.5 μm . and 10-16 μm . were used. Before use, the support was ground for smooth surface. After that it was cleaned with diluted, hot hydrochloric acid, followed by rinsing with deionized water several times. Then, it was cleaned by boiling in xylene for thirty minutes, subsequently with a mixture of H_2O_2 (30%) : NH_4OH (25%) : H_2O = 1 : 1 : 5 parts by volume for fifteen minutes at 80 °C. Finally, it was rinsed with hot deionized water and dried at 170 °C [21]. In case of the silica fiber support, the support was not ground. Other as those of the borosilicate glass disc support treatments of support were the same.

3.1.3.2 Membrane synthesis

The hydrothermal synthesis of a silicalite membrane was performed as follows; Ludox was added to a stirred mixture of tetrapropylammonium bromide (TPABr) and sodium hydroxide solution, to give a hydrogel with a composition of $0.1\text{TPABr}-0.05\text{Na}_2\text{O}-\text{SiO}_2-80\text{H}_2\text{O}$ [7]. Then the hydrogel was placed in Teflon-lined stainless steel autoclave. The support on above was placed in the middle of the autoclave by hanging on the stand as shown in Figure 3.1. The autoclave was placed in hot air oven at $170\text{ }^\circ\text{C}$ for 48 hours. After the completion of crystallization under autogenous pressure without stirring, the autoclave was cooled down and the support was recovered. The silicalite membrane on the support was washed with deionized water and dried at $100\text{ }^\circ\text{C}$. After that the membrane was calcined at $500\text{ }^\circ\text{C}$ for 6 hours with air flow and cooled down.

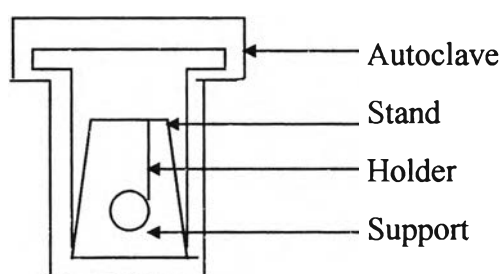


Figure 3.1 The support was placed in the middle of the autoclave by hanging on the stand.

3.2. Membrane characterization

The membrane was characterized by the following techniques:

3.2.1 Thermogravimetric Analysis (TGA) [22]

Thermogravimetric analysis was used to determine the suitable temperature for the decomposition of the templates inside the pores of silicalite membrane, and for the calcination. The experiments were carried out on a Netzsch type STA 409C

Simultaneous Thermoanalyzer under a flow of argon in the temperature ranges of 25-820 °C with a heating rate of 10 °C/min.

3.2.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used particularly for the examination of the topology of catalyst surfaces and the morphology of particles and crystals [23]. The experiments were carried out on a Jeol type 6400 Scanning Microscope.

3.2.3 X-ray Diffraction (XRD)

X-ray Diffraction was used to indicate the uniqueness in structure, as the diffraction pattern is a fingerprint of individual zeolite structures. The XRD measurements were scanned in the ranges of $5^\circ < 2\theta < 60^\circ$. They were performed on a Jeol type JDX 8030 X-ray Diffractometer with a Cu X-ray tube.

3.3. Separation process

The silicalite membrane was synthesized on the support which had been joined with 3-way Pyrex glass tube, called a cell, as shown in Figure 3.2.

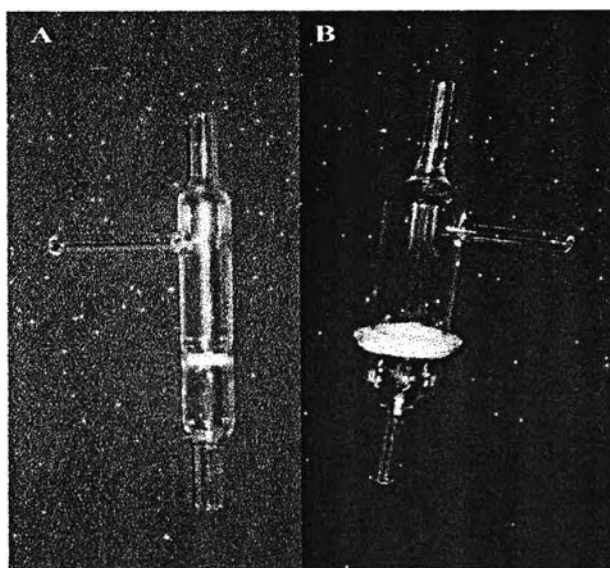


Figure 3.2 The cells for gas separation process. A: joined by gas welding; B: joined by epoxy resin.

This cell was installed outside the gas chromatography (GC) and heated by the heating element. This system is shown in Figure 3.3

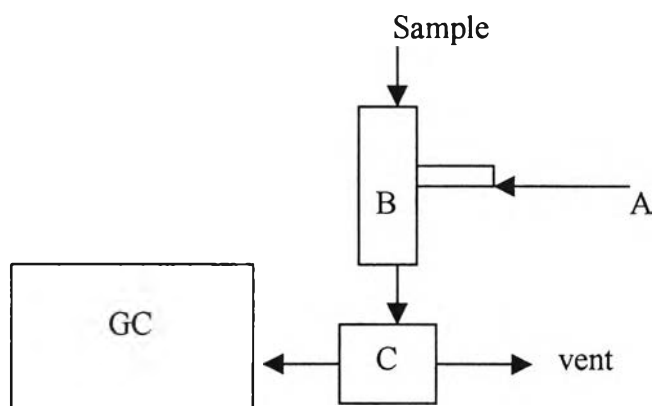


Figure 3.3 Schematic of gas separation process. A: Line of the carrier gas (He); B: cell wrapped by the heating element; C: GC gas sampling valve.

The cell was connected with gas sampling valve and wrapped by the heating element. The conditions of the separation were 140 °C with carrier gas pressure of 1 bar. Mixed xylenes was injected for leak checking. The samples of p-xylene and o-xylene were injected to test the separation performance of this membrane. The permeates flowed through the loop of gas sampling valve, after that, they were injected into the capillary column connecting with the FID detector. The conditions of GC for analysis of the permeates were shown in Appendix A1.

In case of packed column, mixed xylenes which weight ratios of p-, m- and o-xylenes were 1 : 1 : 1, 1 : 2 : 1 and 1 : 1 : 2. The carrier gas pressure was 0.5 bar. The procedures are similar to those in the capillary column. Detectors were TCD and FID. The conditions of GC were shown in Appendix A2.