

Chapter 3

Experimental

3.1 Equipments and Instruments

	Model	Brand
1. Mechanical stirrer	MDC-NS	Eyela
2. Magnetic stirrer	M21/1	Morat
3. Water aspirator	A-3S	Eyela
4. Oven	500	Memmert
5. Carbolite furnaces	GSM	Bamford
6. Programmable temperature controller	PC-600M	Shinko
7. Tube reactor/tube furnace		
8. Schlenk vacuum/gas line		
9. Glove bag		
10. Catalytic unit		
11. GC	9A	Shimadzu
12. X-ray diffractometer	JDX-8030	Jeol
13. FT-IR spectrophotometer	Impact 400	Nicolet

3.2 Chemicals

1. Aluminium sulfate	regent grade	Nacalai Tesque
2. Alumina trihydrate	regent grade	PQ Chemicals (Thailand)
3. Sodium Hydroxide	AR grade	J.T.Baker
4. Sodium silicate solution	$\text{Na}_2\text{O}:3.11\text{SiO}_2$	Thai Silicate
5. Ammonium chloride	AR grade	Fluka
6. NH_4Y zeolite	$\text{Si}/\text{Al} = 2.49$	Aldrich
7. NaY zeolite	$\text{Si}/\text{Al} = 2.37$	Aldrich
8. $\text{Rh}(\text{acac})(\text{CO})_2$	98%	Aldrich
9. n-Hexane	AR grade	Carlo Erba
10. Lithium aluminium hydride	95%	Aldrich
11. 2-Methyl pentane	GC grade	Fluka
12. 1-Butanal	GC grade	Fluka
13. i-Butanal	GC grade	Fluka
14. i-Butanol	GC grade	BDH
15. 1-Butanol	GC grade	Carlo Erba
16. n-Heptane	GC grade	May&Baker
17. 1-Hexene	AR grade	Fluka
18. 1-Heptanal	GC grade	Fluka
19. 1-Heptanol	GC grade	Fluka

20. 2-Heptanol	GC grade	Fluka
21. Acetylacetone	AR grade	Fluka
22. Propylene gas	HP grade	Liquid Carbonic
23. Carbon monoxide gas	HP grade	TIG
24. Hydrogen gas	HP grade	TIG
25. Nitrogen gas	UHP grade	TIG
26. Oxygen gas	HP grade	TIG

3.3 Reagents, Gases and Solvents

Sodium aluminate solution (Reagent A; 23.13% Na_2O , 4% Al_2O_3 , by weight). An amount of 23.44 g alumina trihydrate was dissolved in 114.75 g boiled solution of sodium hydroxide in 243.75 cm^3 water. The mixture is heated continuously until well uniformed and cooled to room temperature before using.

Sodium aluminate solution (Reagent B; 22.59% Na_2O , 20.27% Al_2O_3 by weight). Similarly to preparation of Reagent A, an amount of 15.50 g alumina trihydrate was dissolved in a boiled solution of 14.57 g sodium hydroxide in 19.93 cm^3 water.

Aluminium sulfate solution (Reagent C; 28.21% $\text{Al}_2(\text{SO}_4)_3$, 71.79% H_2O by weight). An amount of 36.67 g aluminium sulfate dihydrate was dissolved in 93.33 cm^3 water.

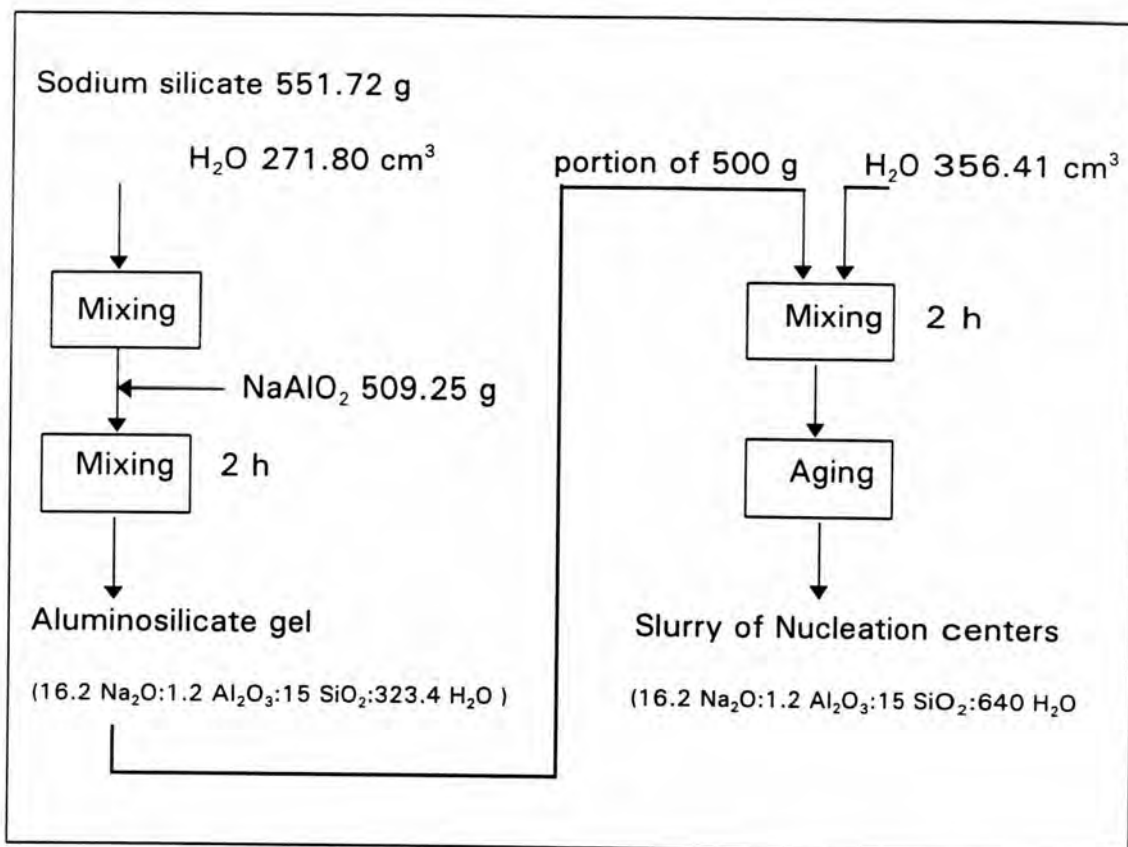
Gases. All gases were passed through moisture traps containing granular drierite and molecular sieve 4A to remove traces of moisture.

Solvents. All solvents were deoxygenated and dehydrated prior to use. The n-hexane was refluxed over LiAlH_4 powder under nitrogen atmosphere for 3 h and transferred to a Schlenk storage tube. n-Decane was degassed and dried over Molecular Sieves 4A.

3.4 Preparation of Zeolite Y

3.4.1 Preparation of the Nucleation Centers

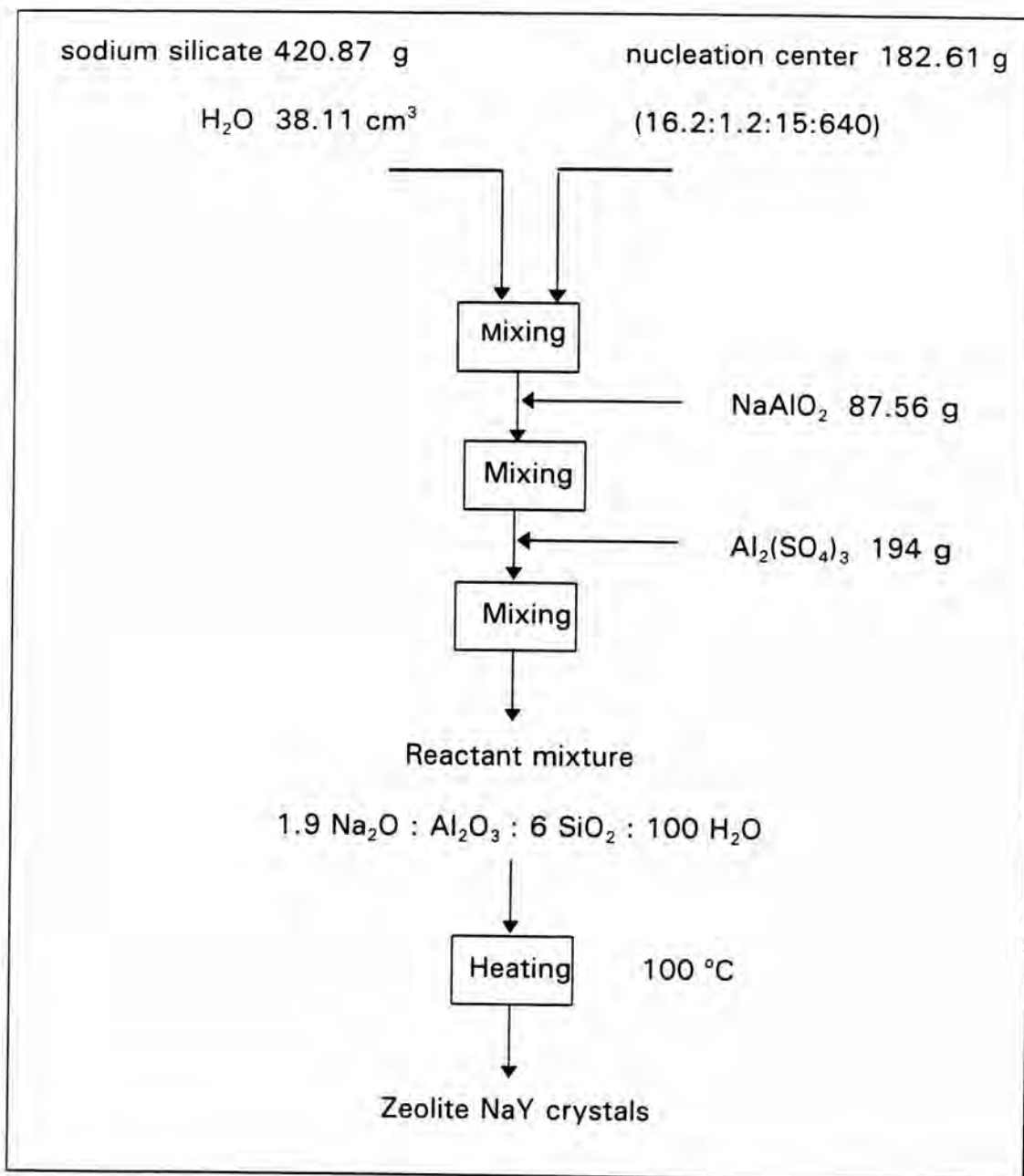
An amount of 509.25 g sodium aluminate solution (Reagent A) was added into a mixture of 551.72 g sodium silicate containing 8.99% Na₂O and 27.09% SiO₂ by weight in 271.8 cm³ water. The mixture was agitated vigorously for 2 h at room temperature. After mixing the mixture became a concentrated milkyl gel containing 4-component mole ratio as 16.2Na₂O:1.2Al₂O₃:15SiO₂:320.4H₂O. An amount 500 g of the concentrated milkyl gel was diluted with 356.41 cm³ water. Then the diluted milkyl gel having composition of 16.2Na₂O:1.2Al₂O₃:15SiO₂:640 H₂O was agitated vigorously for 2 h and aged in a sealed vessel for a different period of time at room temperature to form nucleation centers. After one day, the diluted milkyl gel became two separated phases of precipitate and liquid. Effect of aging time on the crystal formation of zeolite NaY will be studied. Scheme 3.1 illustrates the diagram of preparing the nucleation centers.



Scheme 3.1 : The steps of preparing the nucleation centers having the composition of $16.2 \text{ Na}_2\text{O} : 1.2 \text{ Al}_2\text{O}_3 : 15 \text{ SiO}_2 : 640 \text{ H}_2\text{O}$.

3.4.2 Preparation of Zeolite NaY Crystals

A reaction mixture having mole ratio of $1.9\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:6\text{SiO}_2:100\text{H}_2\text{O}$ was prepared by adding 182.61 g nucleation centers into the solution of 420.87 g sodium silicate and 38.11 cm^3 water. The mixture was stirred vigorously until homogeneous. An amount of 87.56 g the sodium aluminate solution (Reagent B) was slowly added and mixed continuously. Then 194 g of aluminium sulfate solution was added. The mixture was agitated strongly for 2.50 h to obtain homogeneous mixture. The gel was heated in an oven at $100\text{ }^\circ\text{C}$. Various periods of crystallization were studied. After the desired crystallization time, the solids were separated from the mother liquor by filtration and washed with distilled water until the filtrate was base-free. The solid was dried at $105\text{ }^\circ\text{C}$ and ground finely. The powders were characterized by X-ray powder diffraction technique. Scheme 3.2 illustrates the diagram of preparing zeolite Y from reactant slurry having composition of $1.9\text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 6\text{ SiO}_2 : 100\text{ H}_2\text{O}$.



Scheme 3.2 : The diagram of preparing zeolite Y from the nucleation centers and a reactant slurry having composition of 1.9 Na₂O : Al₂O₃ : 6 SiO₂ : 100 H₂O.

3.4.3 Calculation for Preparation of the Nucleation Centers and Reaction Mixture

Table 3.1 to 3.3 show how to calculate for amount of materials used to prepare the nucleation centers and the reaction mixture.

Table 3.1 : Components in preparation of the nucleation centers having the oxide ratio 16:1.2:15:320.

Material	Weight (g)	MW	Na ₂ O 62	Al ₂ O ₃ 102	SiO ₂ 60	H ₂ O 18
Al ₂ O ₃ . 3 H ₂ O	31.25	156	-	0.2	-	0.6
NaOH	153	40	1.9	-	-	1.9
H ₂ O	325	18	-	-	-	18.1
Sodium silicate (Na ₂ O:3.11 SiO ₂) 8.99 % Na ₂ O 27.09% SiO ₂ 59.15% H ₂ O	551.72		0.8	-	2.5	18.2
H ₂ O	271.8	18	-	-	-	15.1
Sum	1332.77		2.7	0.2	2.5	53.9
Molar ratio			16.2	1.2	15.0	323.4

Table 3.2 : Components in preparation of the nucleation centers having the oxide ratio 16:1.2:15:640.

Material	Weight (g)	MW	Na₂O 62	Al₂O₃ 102	SiO₂ 60	H₂O 18
Nucleation centers (16.2: 1.2: 15: 323.4)	500		1.01	0.08	0.94	20.22
H₂O	356.41	18	-	-	-	19.80
Sum	856.41		1.01	0.08	0.94	40.02
Molar ratio			16.2	1.2	15.0	640

Table 3.3 : Components in preparation of the reaction mixture having the oxide ratio 1.9:1:6:100.

Material	Weight (g)	MW	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O
			62	102	60	18
Nucleation centers (16.2:1.2:15:640)	182.61		0.22	0.02	0.20	8.53
Sodium silicate (Na ₂ O:3.11 SiO ₂)	420.87		0.61	-	1.9	13.83
NaAlO₂ solution 22.59% Na ₂ O 20.27% Al ₂ O ₃ 57.15% H ₂ O	87.56		0.32	0.17	-	2.78
H₂O	38.11	18	-	-	-	2.12
Al₂(SO₄)₃ solution 28.21% Al ₂ (SO ₄) ₃ 71.79% H ₂ O	194		-0.48	0.16	-	7.74
Sum	923.10		0.67	0.35	2.1	35
Molar ratio required			1.9	1	6	100

From Table 3.3, the initial reactants are prepared in excess soda, so that aluminum sulfate is used to adjust the soda level required for synthesis of zeolite NaY by neutralization. At the same time, the addition of the aluminum sulfate also increases the alumina content to the level required to produce zeolite NaY. Therefore, it can be written as :



3.4.4 Preparation of Zeolite NH_4Y

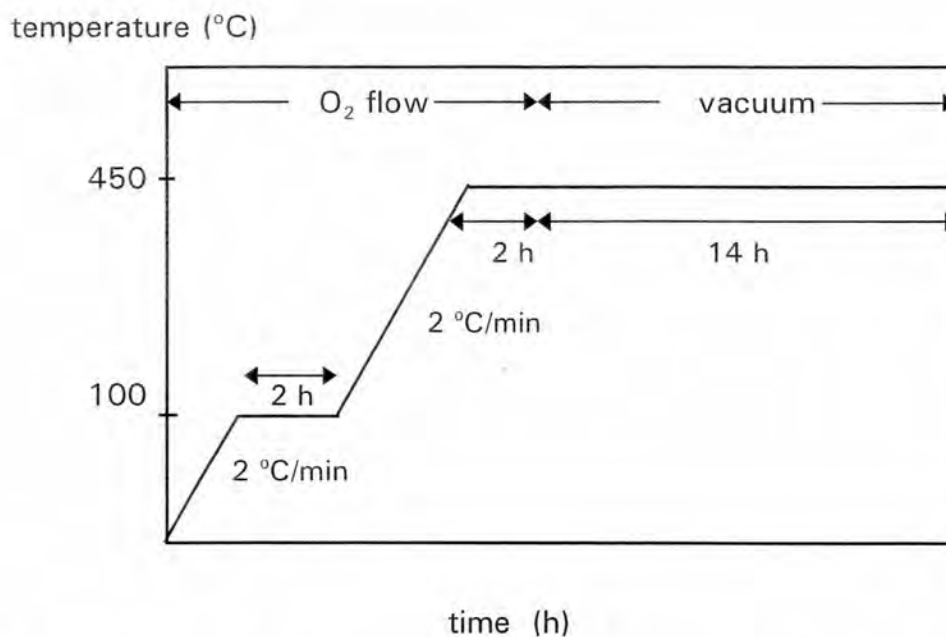
An amount of 10 g NaY was first ion exchanged with ammonium chloride solution (0.04 N) at boiling temperature for 12 h. The zeolite was washed with deionized water to remove chloride ion and then dried in an oven at 105 °C for 1 h. The zeolite NaNH_4Y was calcinated at 540 °C for 3 h to release remained sodium ion from inaccessible positions (site I) to sites which are more accessible to the incoming ammonium cations. The zeolite was secondly and thirdly exchanged with ammonium chloride solution. After each thermal activation of Na ions, the fully exchanged zeolite NH_4Y was filtered, washed and characterized by IR spectroscopy and XRD.

3.5 Synthesis of the Hybrid Catalyst from Rh(acac)(CO)₂ and Zeolite Y

3.5.1 Dehydration of Zeolite Y

The ammonium zeolite ((NH₄)₄₅Na₁₀[(AlO₂)₅₅·(SiO₂)₁₃₇].235H₂O) was heated under oxygen flow at 100 °C for 2 h and at 450 °C for 2 h and then under vacuum at the same temperature for 14 h (at a rate of 2 °C/min) to zeolite HY. The heating diagram for preparation of dry zeolite HY is shown in Scheme 3.3. After cooling to room temperature under vacuum, the dehydrated zeolite HY was then exposed to nitrogen atmosphere.

Zeolite powders (Na₅₇[(AlO₂)₅₇·(SiO₂)₁₃₅].235H₂O) were dehydrated under vacuum at 100 °C for 2 h and at 450 °C for 16 h (rate of 2 °C/min). The dehydration system is shown in Figure 3.1 and the heating diagram for dehydration of zeolite was shown in Scheme 3.4. After cooling to room temperature under vacuum, the dehydrated zeolite NaY was then exposed to dry nitrogen atmosphere.



Scheme 3.3 : The heating diagram for preparation of dry zeolite HY.

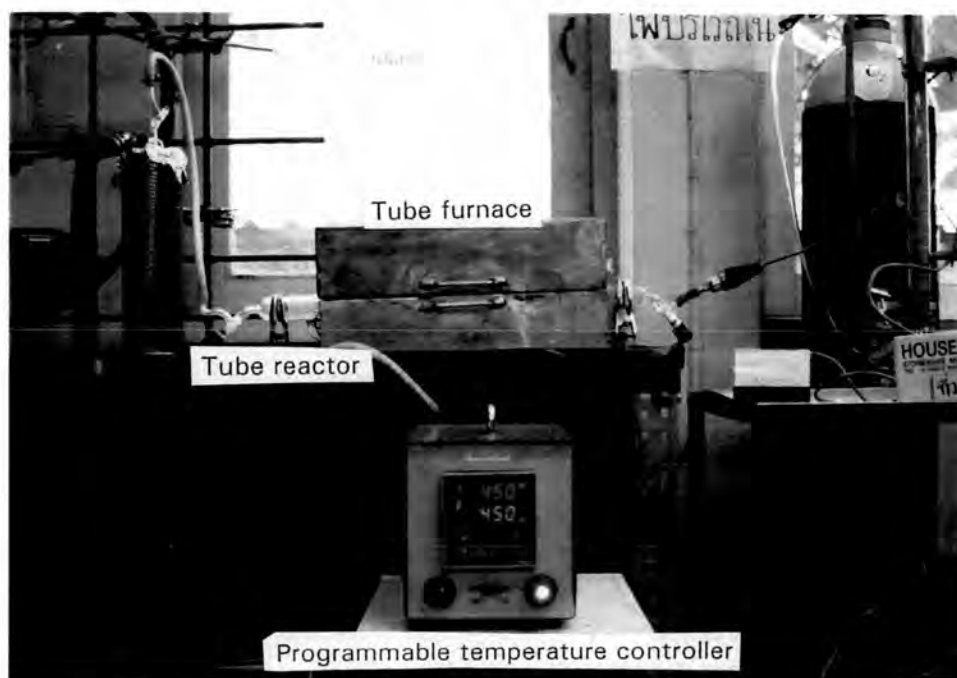
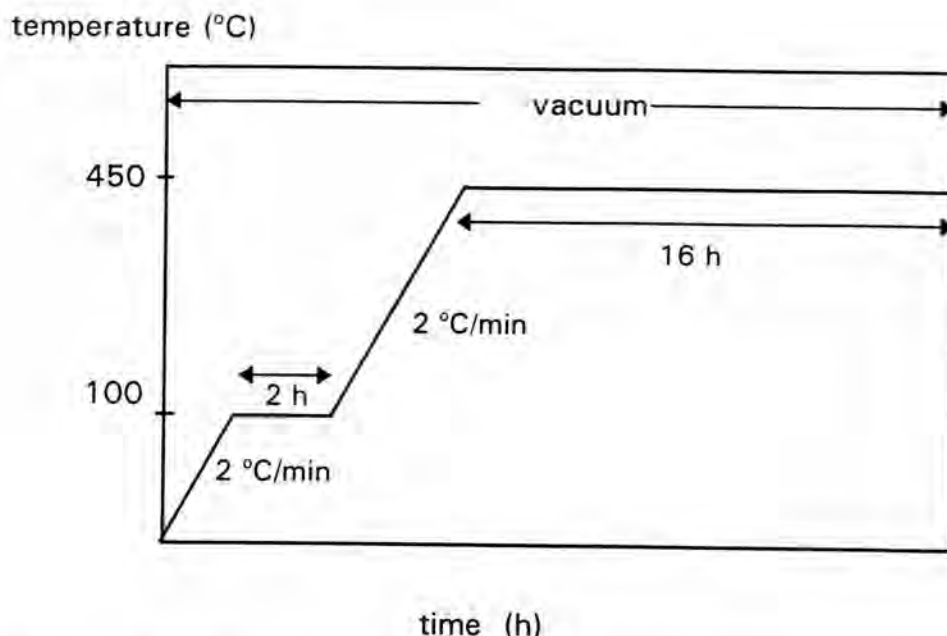


Figure 3.1 : A system for preparation of dehydrated zeolites.



Scheme 3.4 : The heating diagram for dehydration of zeolite NaY.

3.5.2 Anchoring of $\text{Rh}(\text{acac})(\text{CO})_2$ to the Zeolites HY and NaY

The following process was carried out under nitrogen atmosphere using Schlenk technique and a glove bag. The Schlenk gas/vacuum apparatus and the nitrogen glove bag are shown in Figures 3.2 and 3.3. An amount of 1 g of dried zeolite HY or NaY was loaded with 0.5 molecule of $\text{Rh}(\text{acac})(\text{CO})_2$ per supercage in 50 cm^3 of dried n-hexane and the slurry was stirred in a 250 cm^3 Schlenk flask at room temperature for 15 h. The solids were filtered and washed several times with dried n-hexane until no color in the filtrate. The trace n-hexane was removed from the solids via vacuum. The dry solids were then characterized by FT-IR spectroscopy.

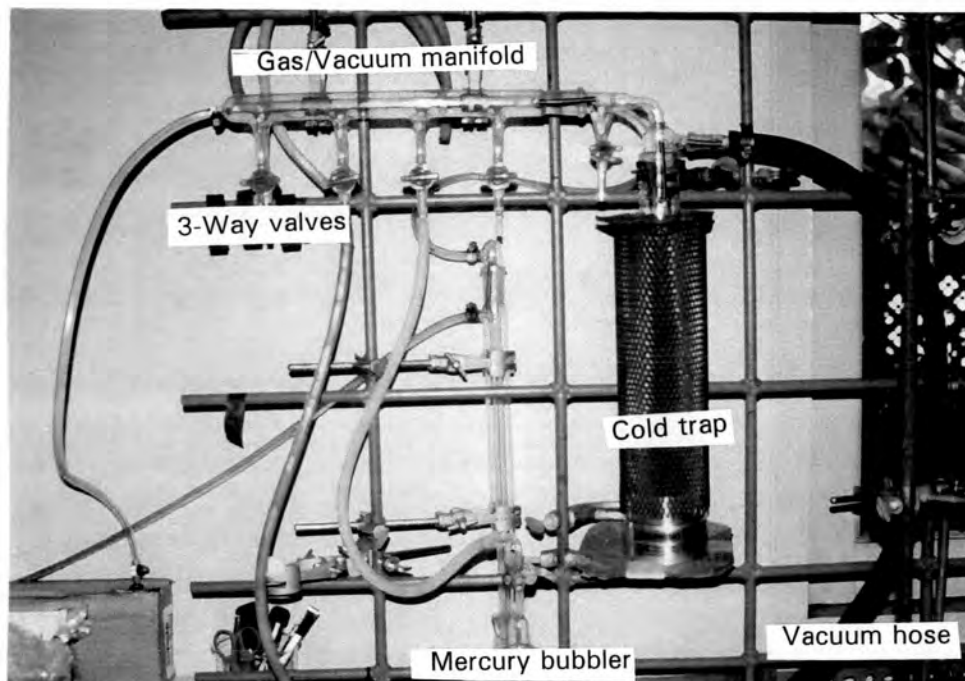


Figure 3.2 : Schlenk line.

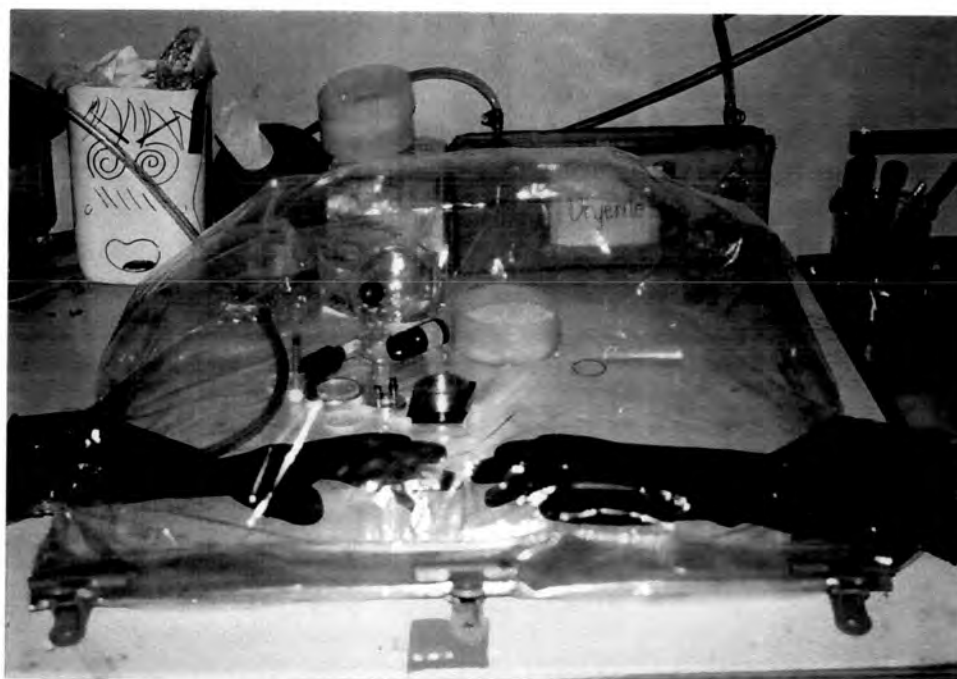
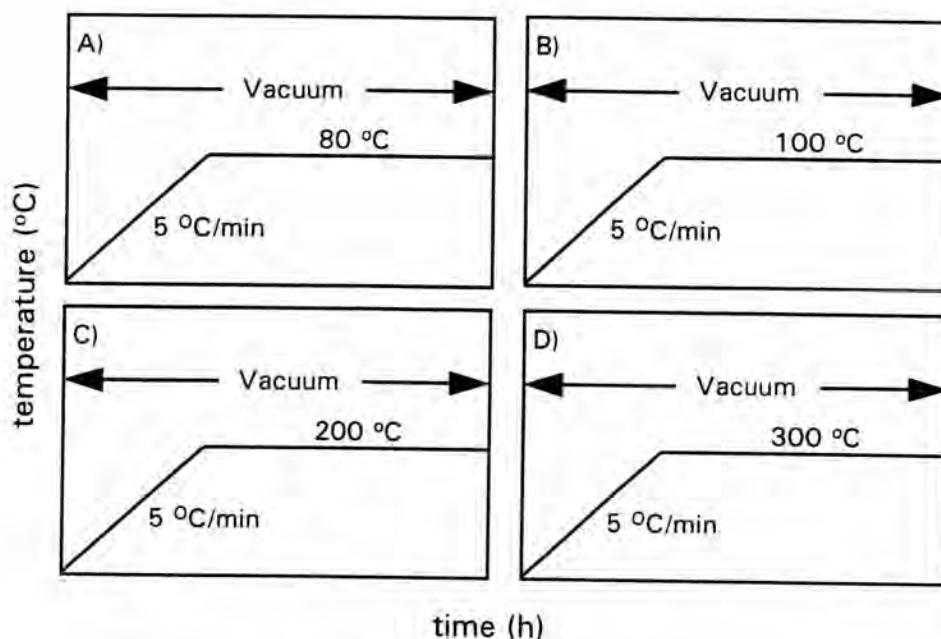


Figure 3.3 : Glove bag.

3.5.3 Thermal Stability of $\text{Rh}(\text{acac})(\text{CO})_2$ on the Zeolite HY and NaY Surface

Thermal stability of the anchored products was examined by heating the sample in the tube furnace under vacuum at different temperatures. The heating diagrams for thermal stability studies are shown in Scheme 3.5. Each temperature was ramped up at the heating rate of $5\text{ }^\circ\text{C}/\text{min}$ to the desired temperature and kept constant for 3 h. After cooling to room temperature under vacuum, the sample was then open to dry nitrogen. The IR samples were prepared by mixing the sample and fluorolube, 2:1 weight ratio, in the glove bag.



Scheme 3.5 : The heating diagram for thermal stability studies : A = 80 °C; B = 100 °C; C = 200 °C; D = 300 °C.

3.6 Catalytic Activity Test for Hydroformylation of Olefins

3.6.1 Propylene Hydroformylation

3.6.1.1 Continuous Feed System

A continuous-feed catalytic system (Figure 3.4) is composed of four gas flowmeters, a U-shape reactor, and a cold trap sitting in a liquid nitrogen bath. An amount of 0.5 g of each zeolite loaded $\text{Rh}(\text{acac})(\text{CO})_2$ was transferred into the reactor under nitrogen. The feeds of propylene, hydrogen, carbonmonoxide, and nitrogen gases were passed continuously through the U-shape reactor at the flow rate of 15, 20, 20 and 20 cm^3/min , respectively. This results in the flow rate ratio of $\text{C}_3\text{:H}_2\text{:CO} = 1.5\text{:}2\text{:}2$. The catalytic activity was tested at different temperatures, 30, 80 and 120 °C. After 2 h, the products were withdrawn for GC analysis using a gas tight syringe from 2 points of the catalytic line. One is as gaseous phase at the point between the U-shape reactor and the cold trap, and the other is as condensed phase deposited in the cold trap. The GC condition is shown in Table 3.4.

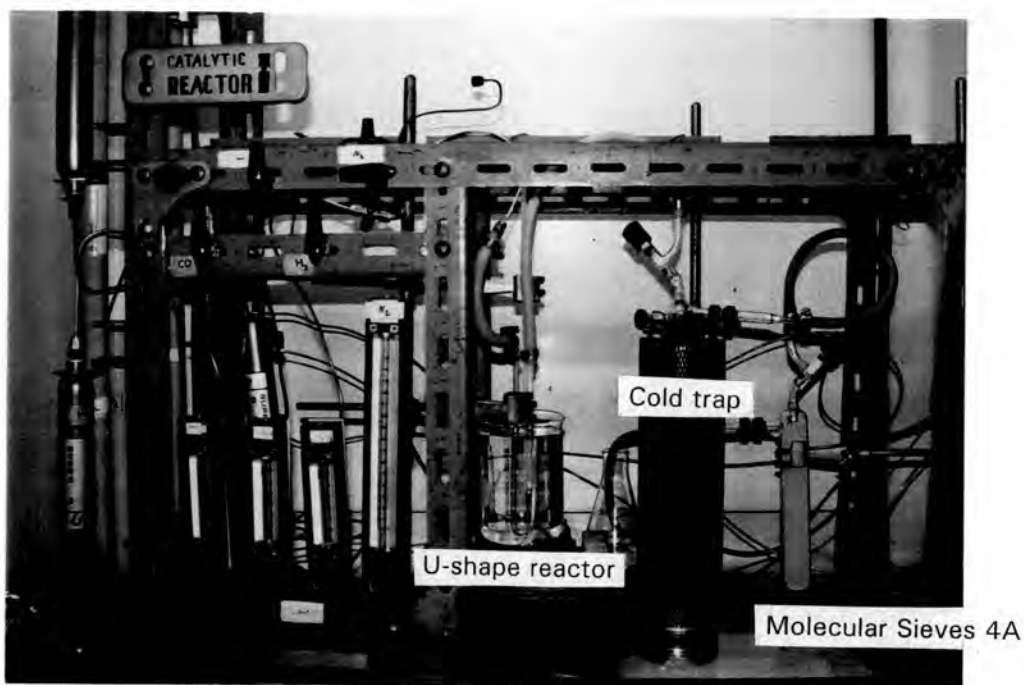


Figure 3.4 : Catalytic system for continuous-feed method.

Table 3.4 : Condition of GC analysis for propylene hydroformylation.

Sample size	:	2 cm ³
Carrier gas	:	N ₂ , 20 cm ³ /min
Injector temperature	:	200 °C
Column	:	Carbowax 20 M, 110 °C
Detector	:	Flame ionization detector, 200 °C
Sensitivity range	:	1

3.6.1.2 Batch System without Vacuum Distillation Technique

This catalytic system is shown in Figure 3.5. An amount of 1 g of each zeolite loaded $\text{Rh}(\text{acac})(\text{CO})_2$ was transferred into a 250 cm³ Schlenk flask under nitrogen. Propylene, hydrogen and carbonmonoxide gases were flew through the flask at the flow rate of 10, 20 and 20 cm³/min, repectively to replace nitrogen gas. This results in the flow rate ratio of $\text{C}_3\text{H}_2:\text{CO} = 1:2:2$. To obtain ambient pressure, the flows were stopped afterwards and the gas outlet was suddently closed using the teflon valve equipped on the Schlenk flask. The catalytic test was performed at room temperature. The gas was withdrawn for GC analysis through a septum on the flask neck for GC analysis once a day until 5 days. The GC condition is shown in Table 3.4.

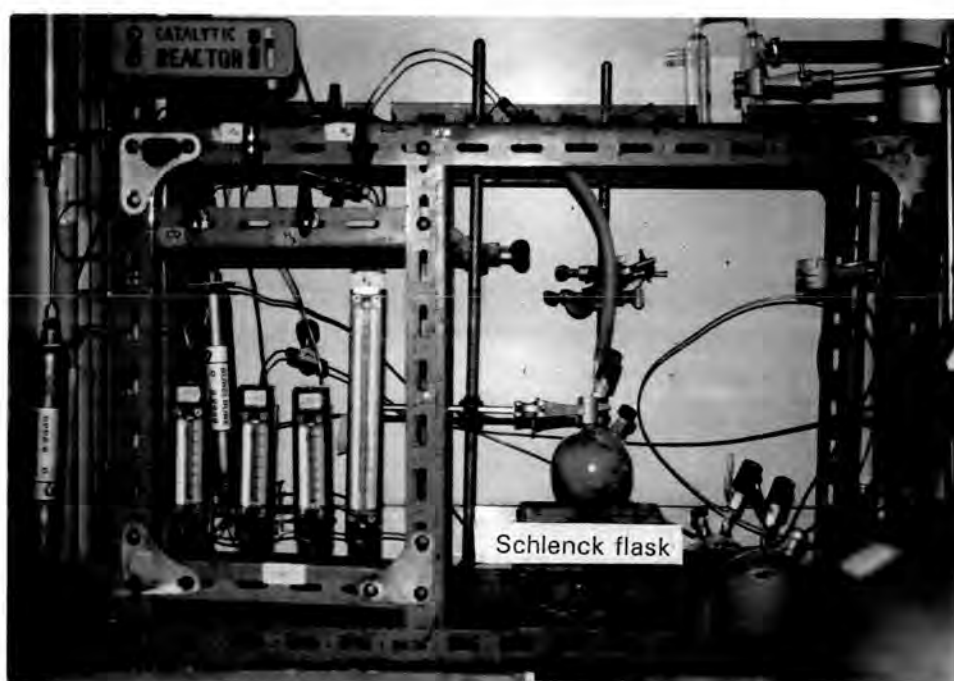


Figure 3.5 : Catalytic system for batch method.

3.6.1.3 Life Time of Catalysts

The apparatus is similar to that in the experiment 3.6.1.2 except the reaction in this system is terminated by vacuum distillation to remove all reagent gases. This is also to remove weakly adsorbed products from the zeolite pores to the cold trap located before the vacuum pump. An amount of 1 g of the zeolite loaded $\text{Rh}(\text{acac})(\text{CO})_2$ was transferred into a 250 cm³ Schlenk flask under nitrogen. Propylene was passed through the flask at the rate of 10 cm³/min. Propylene, carbonmonoxide and hydrogen were flew through the flask at the flow rate ratio of $\text{C}_3:\text{CO}:\text{H}_2 = 1:2:6$. To obtain ambient pressure, the flows were stopped afterwards and the gas outlet was suddently closed using the teflon valve equipped on the Schlenk flask. The catalytic test was performed at room temperature. After 5 days, the volatile products were removed from zeolite pores by vacuum distillation at room temperature, collected in a storage flask cooled by liquid nitrogen, and analyzed by GC. The used catalysts were repeatedly utilized to determine their life time. The used catalysts were analyzed by FTIR spectroscopy and XRD. The condition of GC analysis for propylene hydroformylation is shown in Table 3.4. Numbers of run correspond to times of using the catalysts. For example, run # 1 and 2 means the first and the second times of using the same catalyst.

3.6.1.4 Effect of C₃:CO:H₂ Ratio on Catalytic Activity

The experiment is similar to that in the experiment 3.6.1.3 but using different flow rates of C₃:CO:H₂ = 1:2:2 and 1:4:2. After 5 times repeatedly of the reaction, products were removed from zeolite pores by vacuum distillation at room temperature, collected in a storage flask cooled by liquid nitrogen, and analyzed by GC (condition in Table 3.4).

3.6.2 Hydroformylation of 1-Hexene

An amount of 1 g of each zeolite loaded Rh(acac)(CO)₂ catalyst was put in a 250 cm³ Schlenk flask and pretreated with synthesis gas (CO:H₂ = 1:3) at room temperature for 5 days. An amount of 4 cm³ of 1-hexene in 10 cm³ n-decane(1:2.5 by volume) was syringed into the flask in the ratio of 1 % by weight Rh per substrate. This mixture was then stirred at room temperature for a certain period, and the product in the liquid phase was analyzed by GC. The condition of GC analysis is shown in Table 3.5. Finally, the catalyst was separated from the liquid phase by filtration under nitrogen and the trace liquid phase was removed from the solid via vacuum. Each solid catalyst was characterized using FTIR spectroscopy and XRD.

Table 3.5 : Condition of GC analysis for 1-hexene hydroformylation.

Sample size	:	2 μ l
Carrier gas	:	N ₂ , 30 cm ³ /min
Injector temperature	:	220 °C
Column	:	Carbowax 20 M, 70 °C for 2 min; increased at 20 °C/min to 180 °C; held for 10 min
Detector	:	Flame ionization detector, 220 °C
Sensitivity range	:	10 ³