

## Chapter 4

### Result and Discussion

#### 4.1 Characterization of Zeolite NaY

##### 4.1.1 Characterization of Zeolite NaY with XRD and SEM

In J. Nittayathareekul's report<sup>58</sup>, zeolite NaY was synthesized using hydrothermal method with aging nucleation centers or seeds. The synthesis of zeolite NaY in this project is similar to that reported by J. Nittayathareekul except increasing the speed of the mechanical stirrer from 800 rpm to 1700 rpm. It was found that the crystallization time is shortened from 40 hours to 10 hours while the quality of the products are similar.

After aging the aluminosilicate gel for at least 5 days and the reactants were mixed vigorously using mechanical stirrer, the results of the crystallization of zeolite NaY which were determined by XRD and SEM (Figures 4.1 - 4.3, respectively) are summarized as follows:

(i) Less than 10 hours amorphous phase is still present with the crystalline phase of zeolite NaY. Longer crystallization time reduces the amount of amorphous phase.

(ii) Only zeolite NaY is formed when the crystallization time is between 10 - 15 hours.

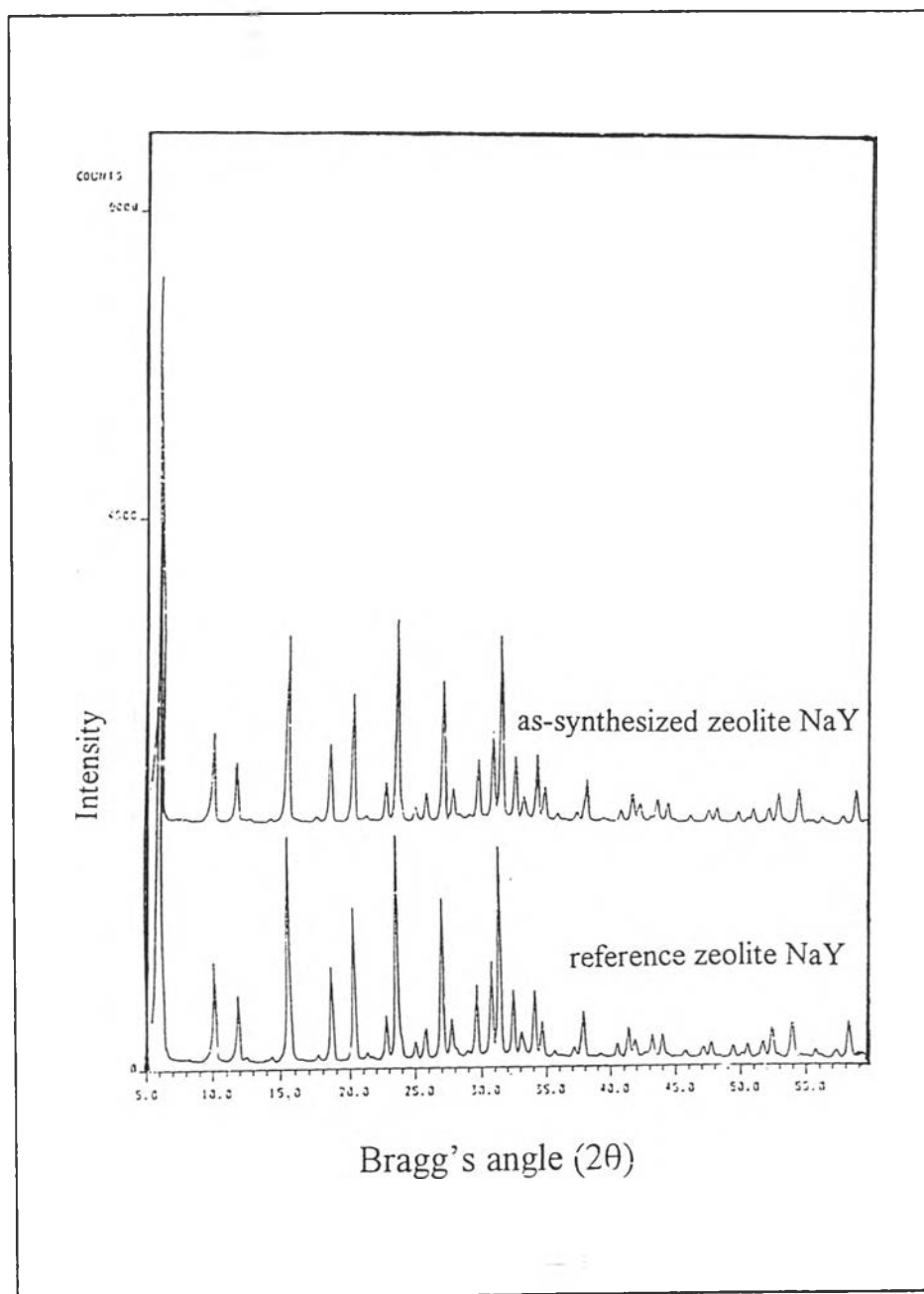


Figure 4.1 XRD patterns of the as-synthesized zeolite NaY and reference zeolite NaY

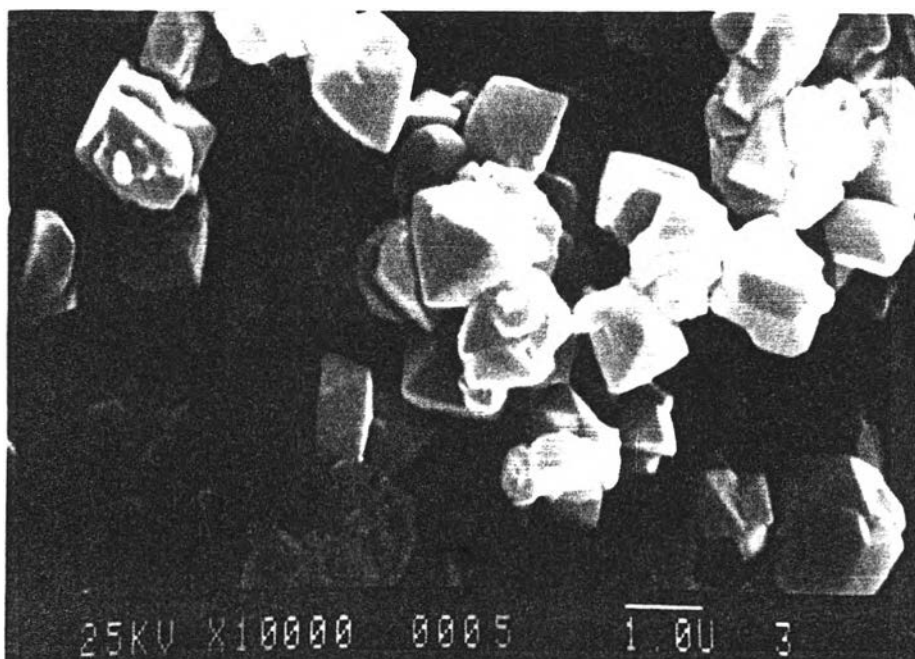


Figure 4.2 Scanning electron micrograph of the as-synthesized zeolite NaY crystals

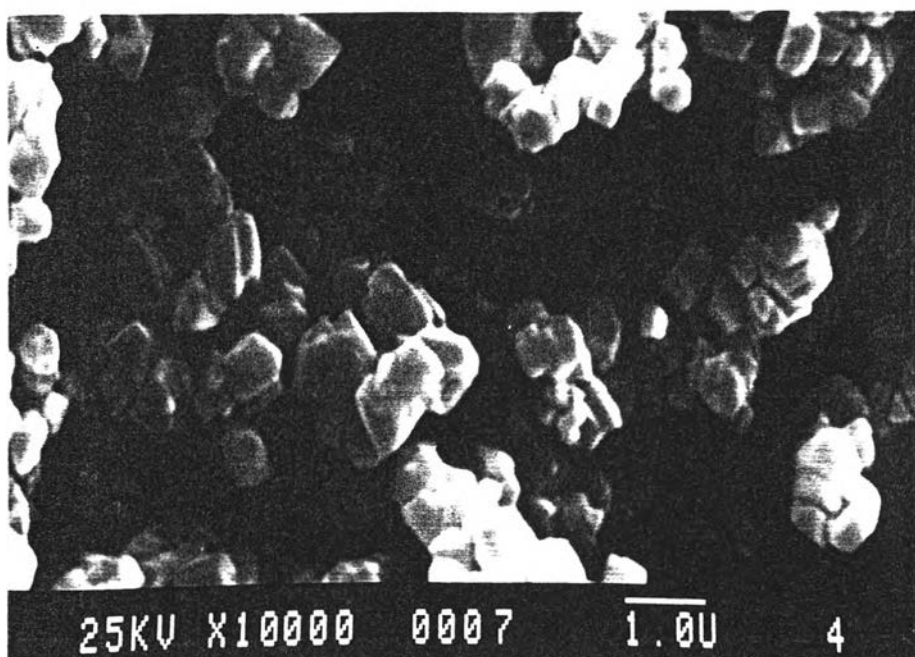


Figure 4.3 Scanning electron micrograph of reference zeolite NaY crystals

(iii) The overlong crystallization time ( $\geq 15$  hours) results in increasing the amount of undesired crystalline phase which is not zeolite NaY.

(iv) The high speed mixing of the reactants gives the well mixed of the reactants and results in shortening of the crystallization time.

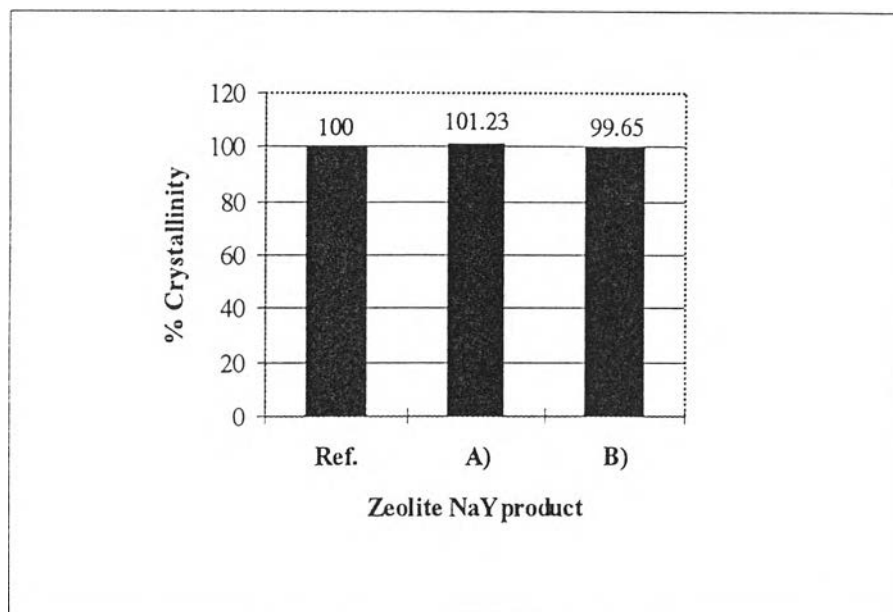
This process is evident that including the room-temperature aging step of the nucleation centers can improve the formation of high crystalline zeolite NaY. The optimum reaction time under the conditions employed in this work was found to include the aging time of the diluted nucleation center  $13.5\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 12.5\text{SiO}_2 : 516\text{H}_2\text{O}$  at least 5 days and crystallization time of the reactant mixture  $1.9\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 6.0\text{SiO}_2 : 100\text{H}_2\text{O}$  added with the nucleation centers about 10 - 15 hours.

The results observed from scanning electron micrograph (SEM) in Figures 4.2 and 4.3 indicated that the as-synthesized zeolite NaY is considerably bigger in crystal size than the reference zeolite NaY obtained from Aldrich. There is no amorphous phase seen around the zeolite crystals.

#### 4.1.2 Percent Crystallinity and XRF Analysis of Zeolite NaY

The as-synthesized zeolite NaY from this work has very high crystallinity up to 99.7 - 101 % and its characteristic XRD pattern is similar to that of reference zeolite. The crystallinity of zeolite NaY is shown in Figure 4.4. The method for determining the percent crystallinity is calculated by:

$$\% \text{crystallinity} = \left( \frac{\sum I_u}{\sum I_s} \right) \times 100 \quad \dots\dots\dots(4.1)$$



**Figure 4.4** Percent crystallinity of zeolite NaY:

Ref = Reference zeolite NaY;

A) = As-synthesized zeolite NaY with aging time 5 days and crystallization time 10 hours;

B) = As-synthesized zeolite NaY with aging time 5 days and crystallization time 15 hours.

Here  $\sum I_u$  and  $\sum I_r$  represent the sum of characteristic peak intensities of sample (synthetic zeolite NaY) and of reference (typical zeolite NaY from Aldrich) at Bragg's angle  $2\theta$  of 10.1, 11.9, 15.6, 18.6, 20.3, 23.6, 27.0, and 31.3 in XRD data. The result shows that the product synthesized in this work has very high crystallinity and in some cases, even higher crystallinity than the reference zeolite. At this point, it should be reminded that different sources of reference may have different levels of crystallinity.

The determination of the formular is based on the concept the summation of all tetrahedron atoms in faujasite structure must be 192 atoms.

$$Al + Si = 192 \dots\dots\dots(4.2)$$

X-ray fluorescence (XRF) analysis shows that the sample contains 56.0 % SiO<sub>2</sub> and 19.1 % Al<sub>2</sub>O<sub>3</sub>. This provides the value of Si/Al ratio as 2.3 and corresponds to the formula of Na<sub>58</sub>[(AlO<sub>2</sub>)<sub>58</sub>.(SiO<sub>2</sub>)<sub>134</sub>].235H<sub>2</sub>O

**4.2 Characterization of Manganese Phthalocyanine Encapsulated in Zeolite Y**

**4.2.1 The Stability of Zeolite Structure on the Amount of Manganese**

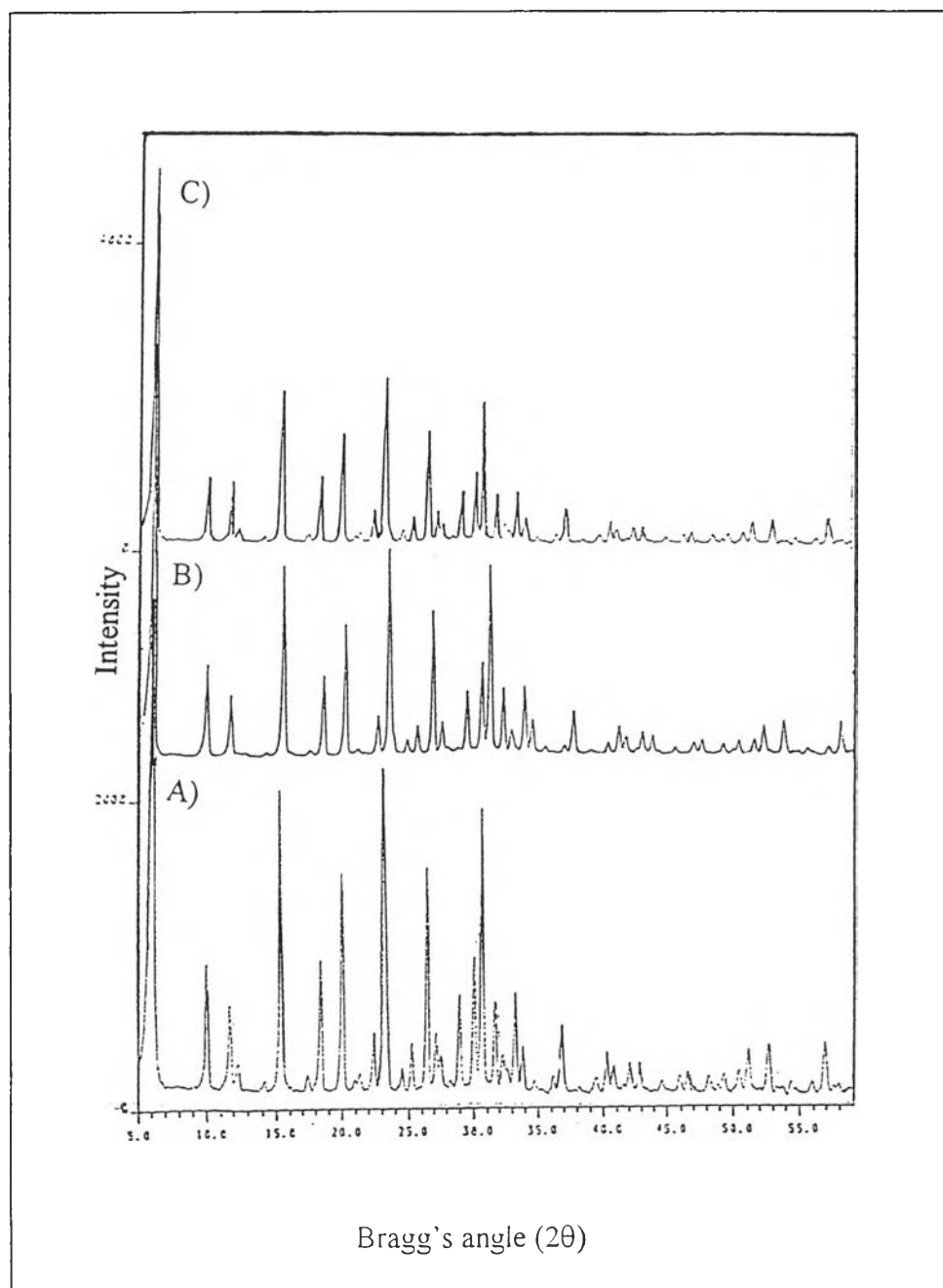
**Loading**

Owing to the oxophilicity of manganese, it may have some effects on framework stability during synthesis. The stability of the zeolite structure on percent loading of Mn<sup>2+</sup> (1, 2, and 3 mol Mn<sup>2+</sup> per supercage zeolite) was studied. Zeolite MnY was obtained by ion exchange of zeolite NaY in aqueous solution of manganese (II)

chloride. After the ion-exchange and filtration, the filtrates of all samples were analyzed for  $\text{Mn}^{2+}$  ion by atomic absorption spectrophotometry. Only 0.6 ppm of  $\text{Mn}^{2+}$  ion was found in each solution after the ion exchange. This means that more than 99 % of  $\text{Mn}^{2+}$  ion can replace  $\text{Na}^+$  ion in the zeolite. The x-ray fluorescence analysis confirms that the manganese contents in the exchanged zeolites are similar to the calculated content, *i.e.* 1, 2, and 3 mol  $\text{Mn}^{2+}$ /supercage, respectively. The XRD patterns of zeolite MnY (shown in Figure 4.5) show that the intensities of the XRD peaks decrease when increasing the manganese content. Only the case of 1 mole  $\text{Mn}^{2+}$ /supercage has no change in peak intensity. This indicates that the frameworks of zeolites MnY with 2 and 3 mol  $\text{Mn}^{2+}$ /supercage SC partly collapse due to oxophilicity of manganese and it can abstract some oxygen atoms from the zeolite framework to form discrete manganese oxide.

#### 4.2.2 Characterization of Intrazeolite Manganese Phthalocyanine

The intrazeolite manganese phthalocyanine was firstly synthesized in a quartz tube containing a sample boat. This apparatus is similar to that utilized for zeolite dehydration which was shown in Figure 3.1. The solid mixture of zeolite MnY and 1,2-dicyanobenzene were heated at 270 °C under vacuum. It was found that after heating, 1,2-dicyanobenzene sublimed to the unheated part of the reaction tube and the solid-state reaction cannot take place. Therefore, the reaction tube was modified to a vacuum sealed ampule.



**Figure 4.5** XRD patterns of zeolite NaY containing

A) 1 mol Mn<sup>2+</sup>/supercage;

B) 2 mol Mn<sup>2+</sup>/supercage;

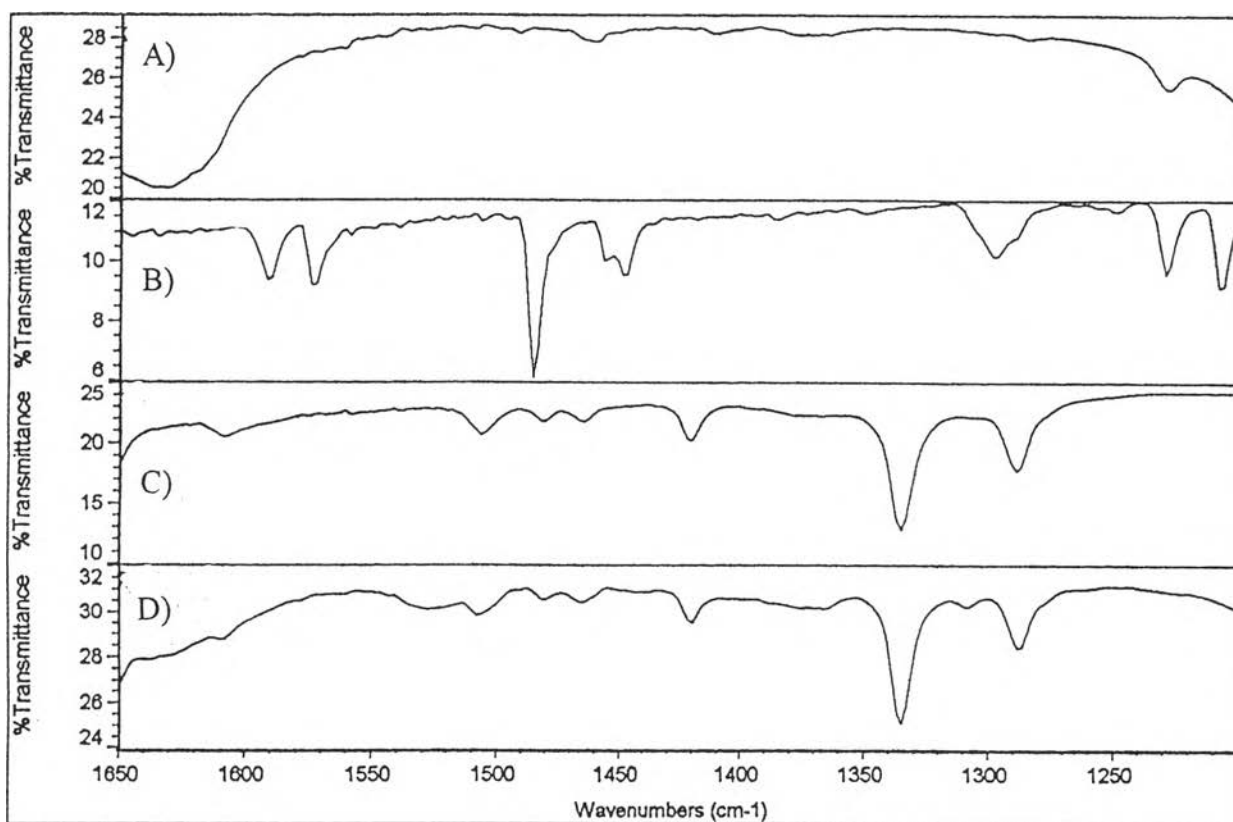
C) 3 mol Mn<sup>2+</sup>/supercage.



The white zeolite MnY reacted with light brown 1,2-dicyanobenzene in vacuum sealed ampule at 270 °C for 40 hours, the solid became greenish-gray. The ampule was open in the glove bag, crude intrazeolite manganese phthalocyanine was washed using soxhlet extraction under nitrogen atmosphere. The first extraction with acetone was performed to eliminate the unreacted 1,2-dicyanobenzene, while pyridine dissolved manganese phthalocyanine or phthalocyanine which formed on outer surface of zeolite. Extraction with acetone in the final step aimed to remove 1,2-dicyanobenzene and pyridine which may be adsorbed in the cavity of zeolite. The infrared spectrum of the greenish-gray manganese phthalocyanine entrapped in zeolite Y shows four bands at 1287, 1336, 1420 and 1508  $\text{cm}^{-1}$  of  $\text{CH}_2$  stretchings (Figure 4.6D). The IR spectrum is comparable with that of the reference manganese phthalocyanine obtained from Fluka (Figure 4.6C and Table 4.1). This indicates the formation of manganese phthalocyanine entrapped in zeolite Y.

**Table 4.1** IR data of transition metal phthalocyanine complexes

complexes	Wave number (1200 - 1650 $\text{cm}^{-1}$ )
Zeolite Y entrapped cobalt phthalocynine (CoPcY)	1290(m), 1333(s), 1426(m), 1523 (s)
Manganese phthalocyanine (MnPc)	1287(m), 1336(s), 1420(m), 1465(w), 1481(w), 1508 (m)
Zeolite Y entrapped manganese phthalocyanine (MnPcY)	1288(m), 1336(s), 1420(m), 1465(w), 1481(w), 1508(m)

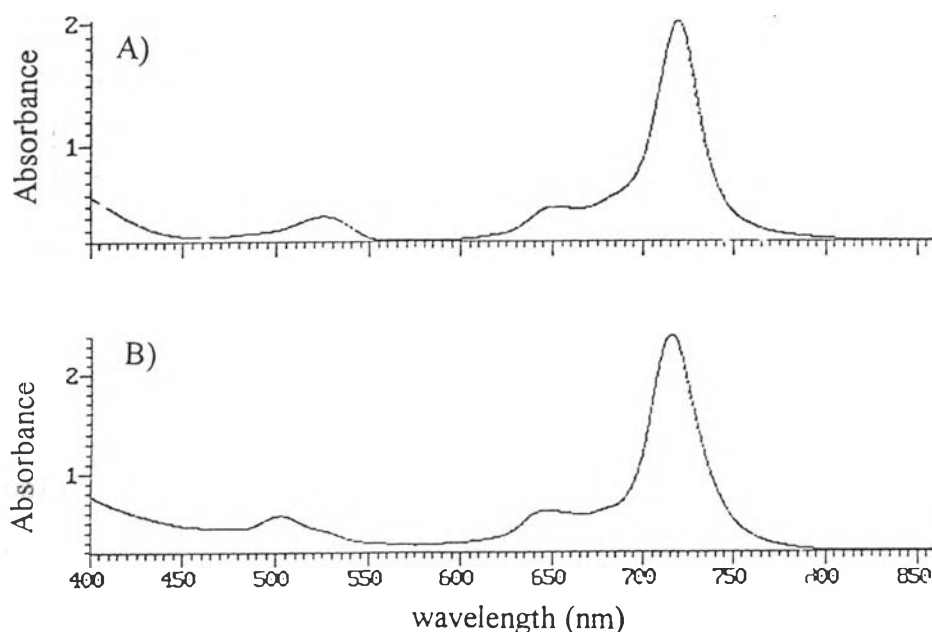


**Figure 4.6** IR spectra (KBr pellets) of

- A) zeolite NaY;
- B) 1,2-dicyanobenzene;
- C) standard manganese phthalocyanine;
- D) manganese phthalocyanine entrapped in zeolite Y.

When MnPcY dissolves in concentrated  $\text{H}_2\text{SO}_4$ , the zeolite structure breaks down and the manganese phthalocyanine migrates to solution, which was characterized by UV-VIS spectroscopy. The absorption bands were observed at 716, 646, and 504 nm which were similar to those absorption bands of standard manganese phthalocyanine purchased from Fluka (Figure 4.7B).

The UV-VIS and IR data confirm coincidentally that the manganese phthalocyanine were successfully synthesized in the cavity of zeolite Y.



**Figure 4.7** UV-VIS absorption spectra of

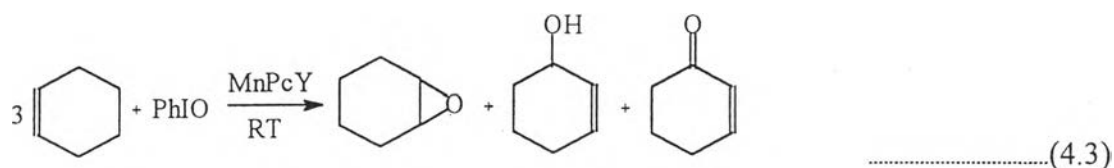
A) manganese phthalocyanine extracted from zeolite Y into conc.  $\text{H}_2\text{SO}_4$ ;

B) reference manganese phthalocyanine in conc.  $\text{H}_2\text{SO}_4$ .

### 4.3 Catalysis on Oxidation of Cyclohexene Using Iodosobenzene as Oxidant

#### 4.3.1 The Tendency of Oxidation Products From Oxidation of Cyclohexene Using Solvent

The catalytic test of the zeolite Y entrapped manganese phthalocyanine was carried out firstly using n-octane as solvent. The catalyst is active for oxidation of cyclohexene even at room temperature, while the oxidation reaction does not take place without the catalyst for each test. The oxidation products are identified by GC-MS as cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one as shown in Equation 4.3.



Along with the formation of oxidation products, phenyl iodide is also found as the major peak in the gas chromatogram in Figure 4.8. The method of the calculation for the quantitative yield of each product, directly withdrawn from the reaction mixture by syringe, is shown in Equation 4.4.

$$\text{mmol of product} = (53 \times A_{\text{sample}} \times 0.004) / (0.5 \times A_{\text{int.std.}}) \quad \dots\dots\dots(4.4)$$

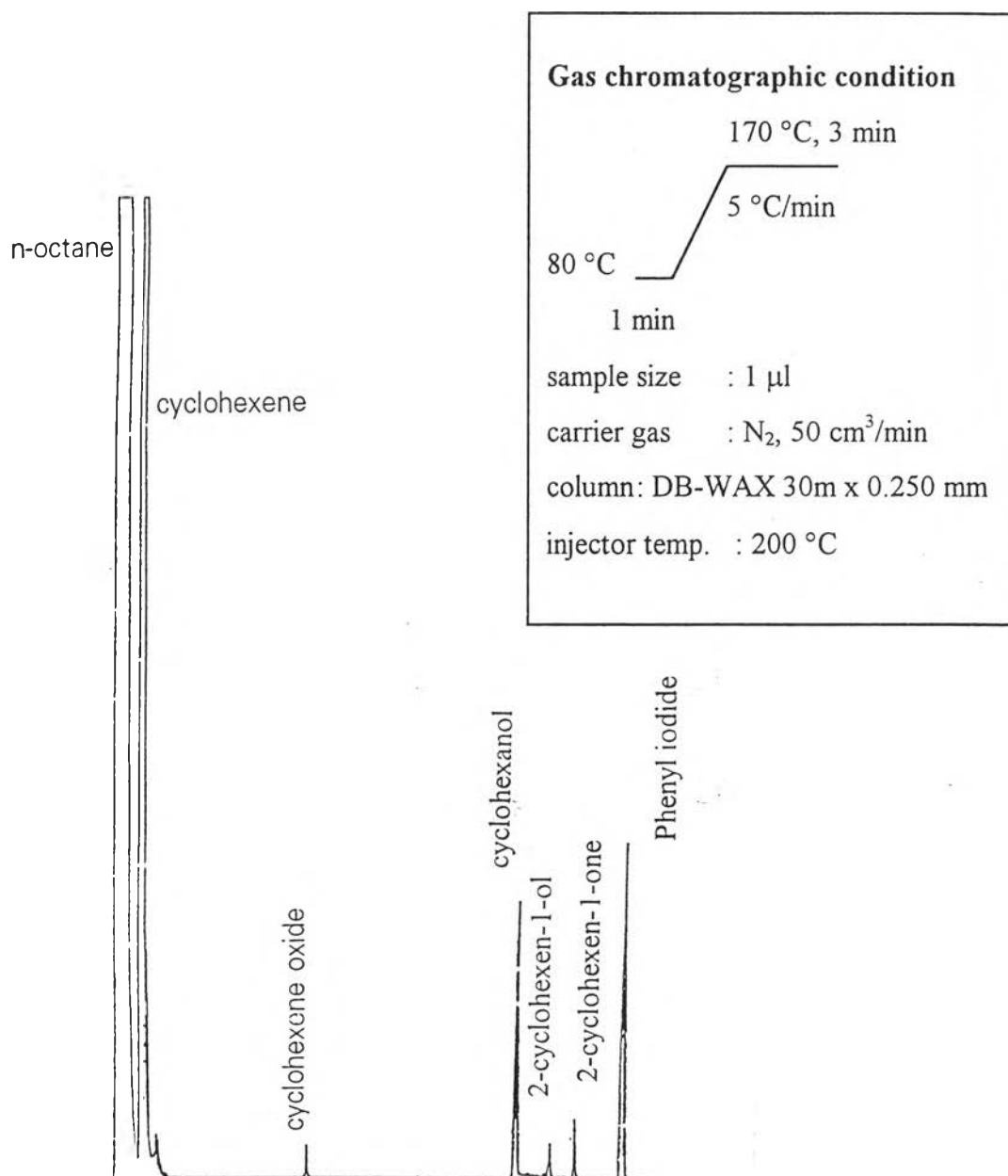
Here: 53 = the total volume of reaction flask (cm<sup>3</sup>).

0.5 = the volume of sample (cm<sup>3</sup>).

0.004 = the known amount of internal standard (mmol).

$A_{\text{sample}}$  = peak area of product peak.

$A_{\text{int.std.}}$  = peak area of internal standard peak.



**Figure 4.8** Gas chromatogram of liquid phase from oxidation of cyclohexene in n-octane using iodosobenzene as oxidant

The catalytic results are compiled in Table 4.2 and Figure 4.9. Considering the curve in Figure 4.9 the data are divided into 2 parts, A and B by the border line at 25 hours. In part A the amount of each product increases at a constant rate. In the first 25 hours, 2-cyclohexen-1-one is the major product and 2-cyclohexen-1-ol and cyclohexene oxide are minor products at similar level. Also, the formation of phenyl iodide (PhI) is observed in a great amount comparing to the three oxidation products. It is found that only the amounts of cyclohexene oxide and phenyl iodide still increase continuously even beyond the border line. This indicates that the oxidation catalysis has not been terminated because the oxidant is still consumed and cyclohexene oxide amount still increases. There is a sudden change for formation of 2-cyclohexen-1-one by decreasing in amount along the passing time after 25 hours. This may be due to the decomposition of the enone. However, there is no other reaction products detected by GC-MS so it is difficult to explain at this moment due to lack of information. The curve of 2-cyclohexen-1-ol in part B maintains at a constant level. This is accounted by either no more production of 2-cyclohexen-1-ol after 25 hours or the equality of rate of formation and rate of decomposition. The results show that selectivity for cyclohexene oxide beyond the border line is better and better upon the passing time.

**Table 4.2** Catalytic activity of zeolite entrapped manganese phthalocyanine for oxidation of cyclohexene in n-octane using iodosobenzene as oxidant

Time (hrs)	Selectivity (%) <sup>a</sup>			Relative amount of PhI <sup>b</sup> (%)	Percent conversion		TON <sup>c</sup>
	cyclohexene oxide	2-cyclohexen-1-ol	2-cyclohexen-1-one		substrate <sup>c</sup>	oxidant <sup>d</sup>	
5	0	41.51	58.49	60.74	0.176	1.64	10
10	24.44	30.00	45.56	63.56	0.300	3.14	10
15	25.30	27.71	46.98	56.32	0.553	4.28	10
20	22.22	27.78	50.00	51.43	0.780	4.96	20
25	21.65	26.80	51.55	50.51	0.970	5.94	20
40	36.76	23.32	39.92	62.90	0.840	8.58	20
50	44.10	25.76	30.13	69.71	0.763	10.54	20

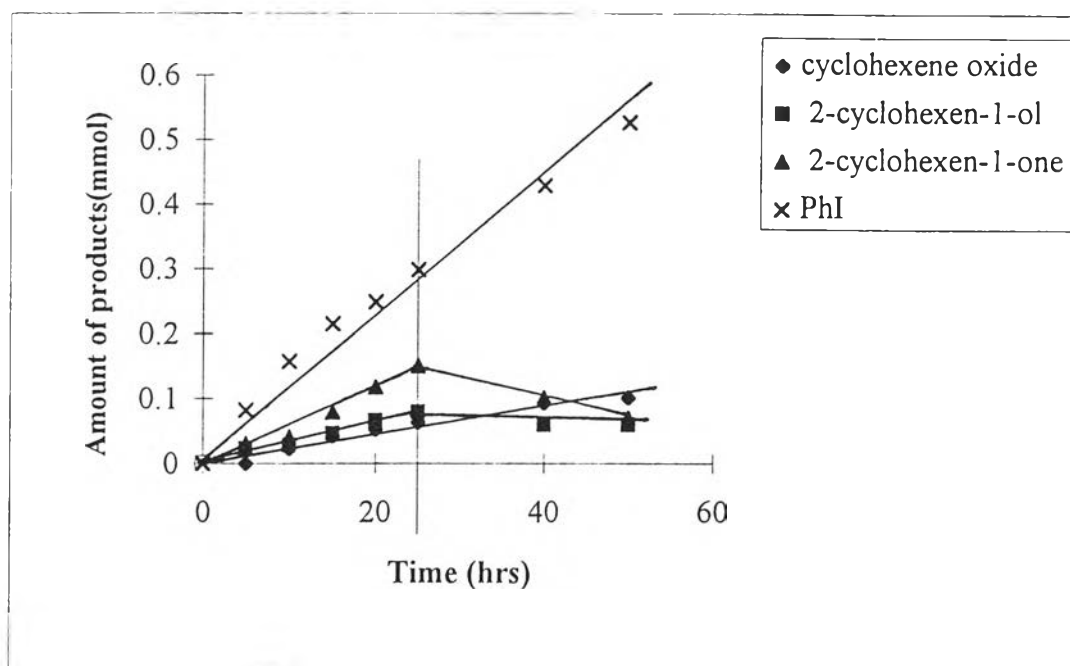
a) Relative yield of each product to total amount of the three oxidation products.

b) 
$$\frac{\text{Amount of PhI}}{\text{Amount of [ PhI + } \text{Cyclohexene oxide} + \text{Cyclohexen-1-ol} + \text{Cyclohexen-1-one} ]} \times 100$$

c) % Conversion based on formation of the three oxidation products.

d) % Conversion based on formation of PhI.

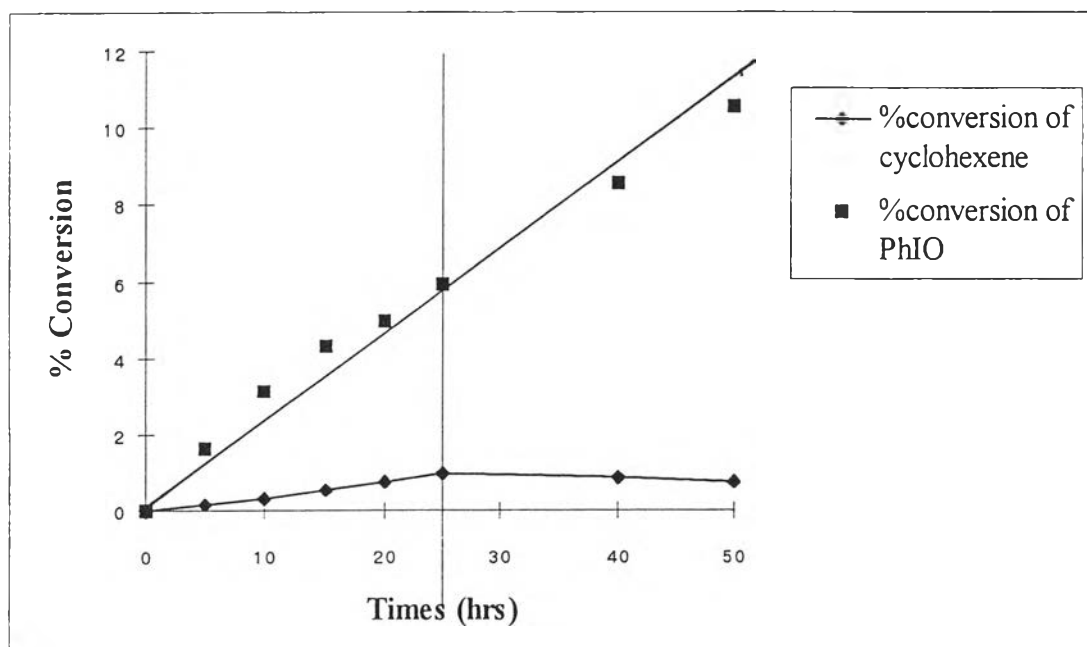
e) Turnover number calculated from mmol of products/mmol of MnPcY catalyst.



**Figure 4.9** The amount of each product from oxidation of cyclohexene in n-octane catalyzed by MnPcY using iodosobenzene as oxidant

Considering Figure 4.10 which shows the change in % conversion of cyclohexene and iodosobenzene calculated from either the total amount of oxidation products or the amount of phenyl iodide. It is obvious that the linearity of the latter is directly relative to the amount of cyclohexene oxide increased in Figure 4.9. This confirms that % conversion of cyclohexene to cyclohexene oxide can actually increase upon increasing reaction time. In contrast, total conversion calculated from the total amount of oxidation products has a break point at 25 hours similar to that found in Figure 4.9. However, to diminish time of catalytic test the catalytic duration is fixed at 24 hours for comparative study of other effects on catalysis.

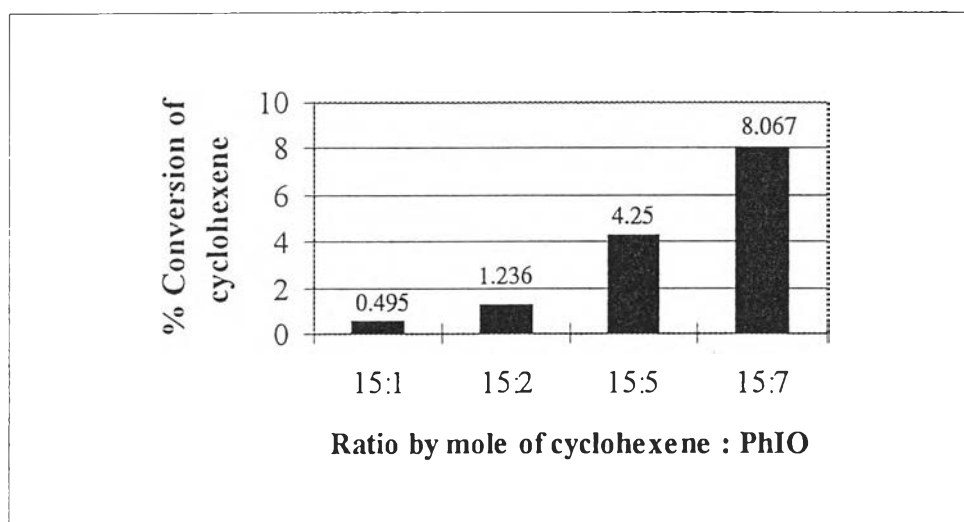




**Figure 4.10** Percent conversions of iodosobenzene and cyclohexene oxidized by iodosobenzene and catalyzed by MnPcY in n-octane

### 4.3.2 Effect of the Amount of Iodosobenzene on Tendency of Oxidation Products From Oxidation of Cyclohexene

It is noticed that highly excess amount of cyclohexene was always used in this project. This is the reason why % conversion based on cyclohexene is very low. It is more reasonable to consider % conversion based on formation of PhI instead, because PhIO is less than the equivalent amount. To increase % conversion of cyclohexene, the effect of amount of oxidant *i.e.* PhIO was also studied and the result is shown in Figure 4.11. It is obvious that there is a drastic change upon increasing the amount of PhIO. However, the large amount of insoluble PhIO provides the trouble of stirring the reaction mixture. Although higher conversion of cyclohexene is achieved, it is still less than 10 %. Therefore, another effect, solvent effect, should be studied to maximize the efficiency of the catalysis.



**Figure 4.11** Effect of the amount of iodosobenzene on oxidation of cyclohexene, 15 mmol cyclohexene,  $3.14 \times 10^{-3}$  mmol catalyst, 24 hours reaction time, room temperature

### 4.3.3 Oxidation of Cyclohexene Without Solvent

In this part the catalysis is designed similarly to the previous one except no solvent is used. By this we expect that the substrate may quickly access to the active site of catalyst because it has no competition with solvent molecules to diffuse through the pore system of zeolite and reaches the active site easily. We have found that using the ratio of 15 mmol of cyclohexene to 7 mmol PhIO is the best condition for catalysis in solvent. Without solvent the large amount of insoluble PhIO can face the problem of stirring. Therefore, the amount of iodosobenzene was reduced to 2 mmol to avoid the stirring difficulty. Similar to the catalysis in the presence of solvent, the oxidation products identified by GC-MS are cyclohexene oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one along with the formation of phenyl iodide which is found as the major peak in the gas chromatogram in Figure 4.12. The quantitative results for the samples separated by vacuum filtration are calculated from Equation 4.5.

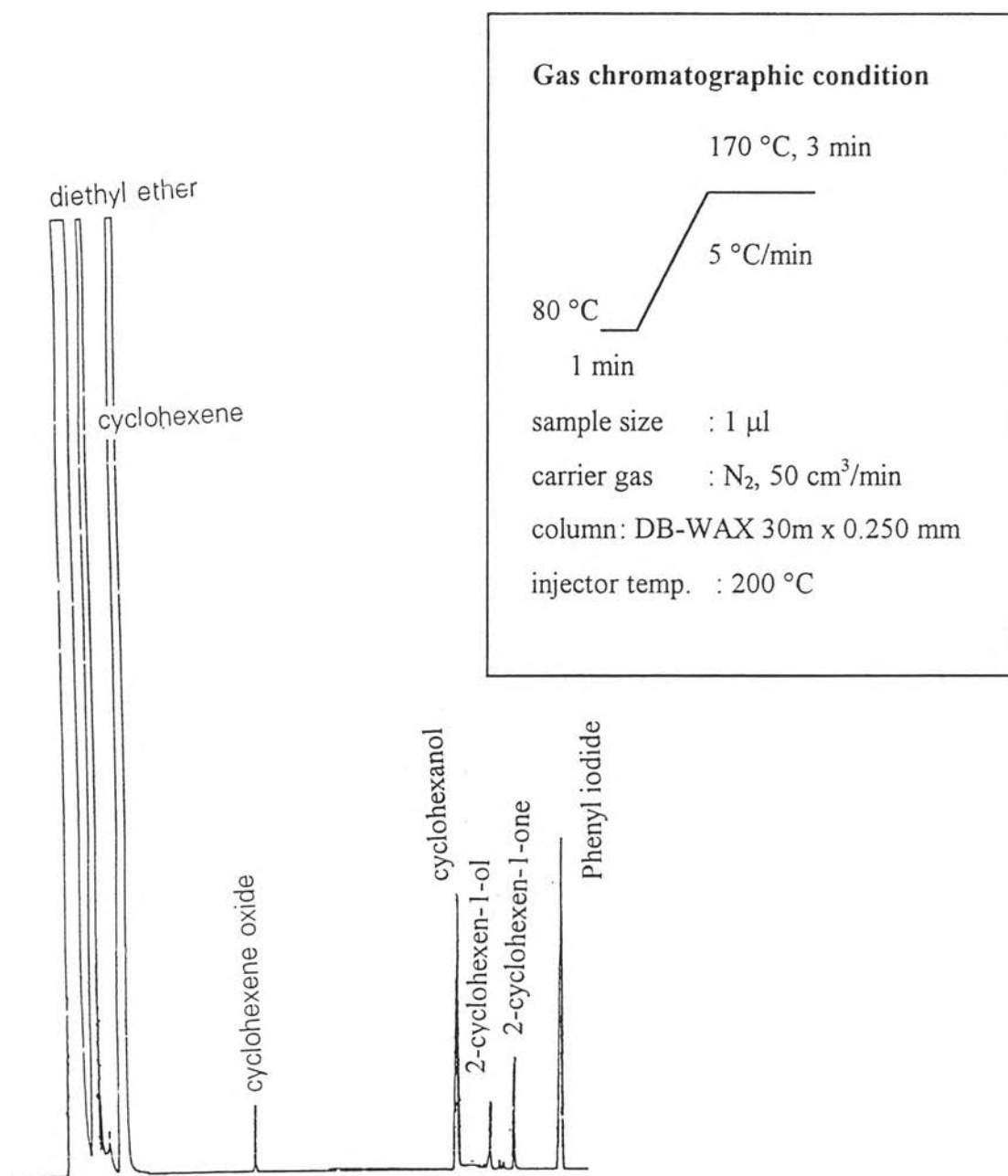
$$\text{mmol of product} = (A_{\text{sample}} \times 0.08) / A_{\text{int.std.}} \times 1.7 \quad \dots\dots(4.5)$$

Here: 0.08 = the known amount of internal standard (mmol).

$A_{\text{sample}}$  = peak area of products peak.

$A_{\text{int.std}}$  = peak area of internal standard peak.

1.7 = correction factor.



**Figure 4.12** Gas chromatogram of liquid phase from oxidation of cyclohexene in the absence of solvent using iodosobenzene as oxidant and MnPcY as catalyst.


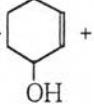
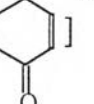
The catalytic result is shown in Table 4.3 and Figure 4.13. % selectivity to cyclohexene oxide increases along with the passing time while the selectivities for the formation of 2-cyclohexen-1-ol and 2-cyclohexen-1-one maintain at a constant level. This is accounted by no more production of 2-cyclohexen-1-ol and 2-cyclohexen-1-one. Similar to the catalysis in the presence of solvent, the selectivity to cyclohexene oxide increases along with the passing time and percent selectivities of 2-cyclohexen-1-ol and 2-cyclohexen-1-one are constant. This result may indicate that in the system which is catalyzed by MnPcY and using iodosobenzene as oxygen donor, the reaction is more selective to the formation of cyclohexene oxide than 2-cyclohexen-1-ol and 2-cyclohexen-1-one.

Considering the profile curves in Figure 4.13, in the first interval of 25 hours the amount of each product significantly increases, similar to the catalysis taking place in n-octane, no significant change after 25 hours. This implies that there is no more products produced after 25 hours, the reaction terminated after 25 hours. The results obtained from the catalysis in the absence of solvent correspond to the results that oxidation taking place in n-octane, cyclohexene oxide is the major product while 2-cyclohexen-1-ol and 2-cyclohexen-1-one are minor products. For 25 hours, the amount of cyclohexene oxide is twice greater than other two oxidation products. However, there is no declination of the profile curve after 25 hours which is in contrast to the catalysis in the presence of solvent.

**Table 4.3** Catalytic activity of zeolite entrapped manganese phthalocyanine for oxidation of cyclohexene in the absence of solvent using iodosobenzene as oxidant and MnPcY as catalyst.

Time (hrs)	Selectivity (%) <sup>a</sup>			Relative amount of PhI <sup>b</sup> (%)	Percent conversion		TON <sup>e</sup>
	cyclohexene oxide	2-cyclohexen- 1-ol	2-cyclohexen- 1-one		substrate <sup>c</sup>	oxidant <sup>d</sup>	
1	15.22	39.13	45.65	58.18	0.153	1.28	20
2	25.00	30.00	45.00	64.71	0.201	2.20	20
3	29.35	27.17	43.48	58.93	0.306	2.64	30
4	23.37	30.00	46.67	65.68	0.200	2.22	20
5	34.62	25.00	40.38	69.41	0.347	4.72	30
6	27.62	32.38	40.00	51.61	0.352	2.24	40
8	31.90	31.17	37.93	56.87	0.389	3.06	40
24	48.03	22.20	29.77	45.37	2.030	10.10	180
48	50.71	21.55	27.74	59.45	1.883	16.74	170

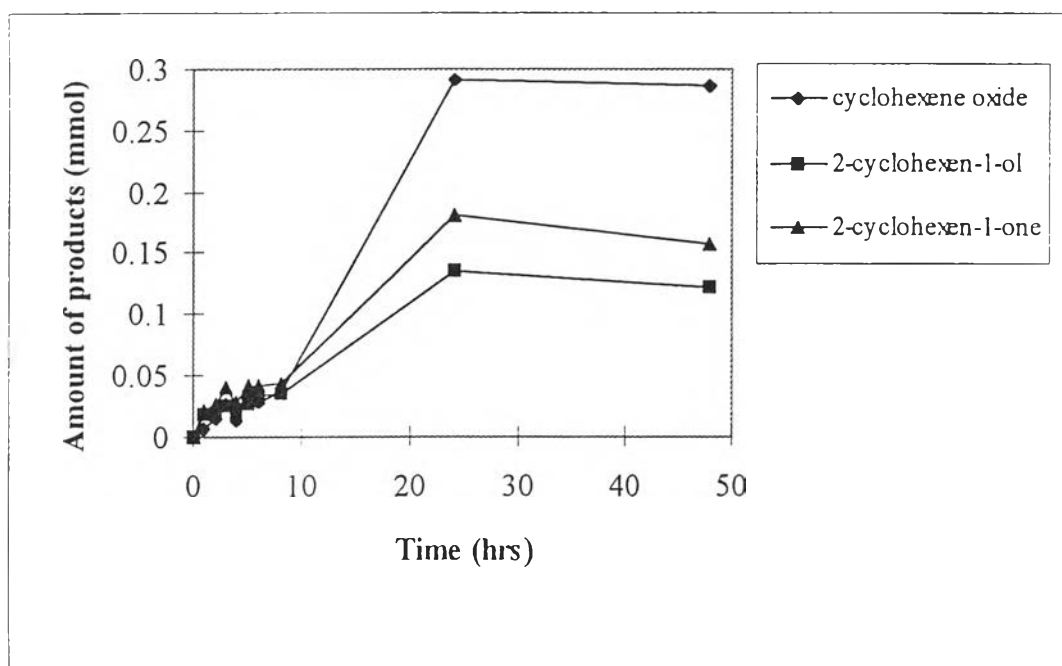
a) Relative yield of each product to total amount of all oxidation product.

b) 
$$\frac{\text{Amount of PhI}}{\text{Amount of [ PhI +  +  +  ]}} \times 100$$

c) % Conversion based on formation of oxidation products.

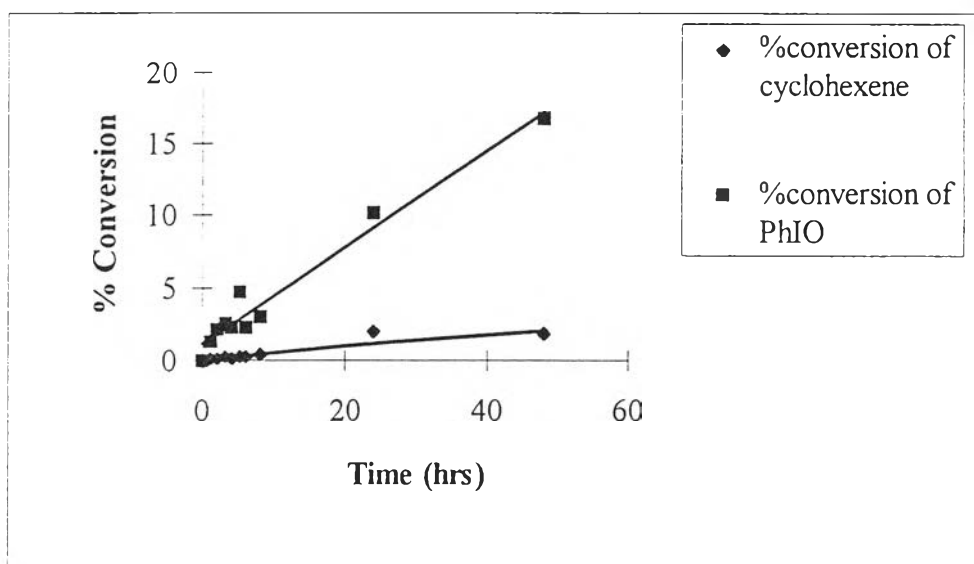
d) % Conversion based on formation of PhI.

e) Turnover number calculated from mmol of products/mmol of MnPcY catalyst.



**Figure 4.13** The amount of each product from oxidation of cyclohexene in the absence of solvent using iodosobenzene as oxidant and MnPcY as catalyst.

Without solvent, % conversion of cyclohexene which is plotted in Figure 4.14, is higher than that in the presence of solvent. This is one advantage of the system that performed in the absence of solvent. It means that our assumption is true: the substrate can reach the active site of the catalyst easily due to no protection of the active site by solvent and the catalysis can take place more easily than that in the presence of solvent. This is also due to solvent effect: hydrophobic solvent may obstruct the attachment of the substrate on the hydrophilic surface of the catalyst.



**Figure 4.14** Percent conversion of cyclohexene oxidized by iodosobenzene and catalyzed by MnPcY without solvent.

However, the reaction in the absence of solvent is limited by the amount of iodosobenzene. It is seen that the amount of iodosobenzene is not exceed 2 mmol when using 30 mmol substrate, this brings about the disadvantage of this system when compared to the system that using solvent which can use the larger amount of oxidant and then provide the high amount of oxidation products.



#### 4.3.4 Effect of the Amount of MnPcY on Oxidation of Cyclohexene

Another way to improve the catalytic activity is to seek for the appropriate amount of the catalyst. In general, only small amount is needed while some other cases may need little larger amount. Effect of the catalyst amount is then studied and the result is shown in Table 4.4 and Figure 4.15. Considering the system using iodosobenzene as oxidant, there is no significant change along with increase of the amount of catalyst. Increasing the amount of catalyst about four times provides the increase of the percent conversion of cyclohexene, two times greater than the system that contained smaller amount of catalyst. This result indicates that amount of catalyst is very important in increasing the % conversion of the catalysis. The larger amount of the catalyst used provides more active site for reaction and finally the oxidation efficiency can be improved.

The result obtained confirms that the catalyst, MnPcY, is selective to the formation of cyclohexene oxide, not to 2-cyclohexen-1-ol or 2-cyclohexen-1-one when PhIO is oxidant.

**Table 4.4** Catalytic activity of different amount of MnPcY for oxidation of cyclohexene for 24 hours without solvent using iodosobenzene as oxidant

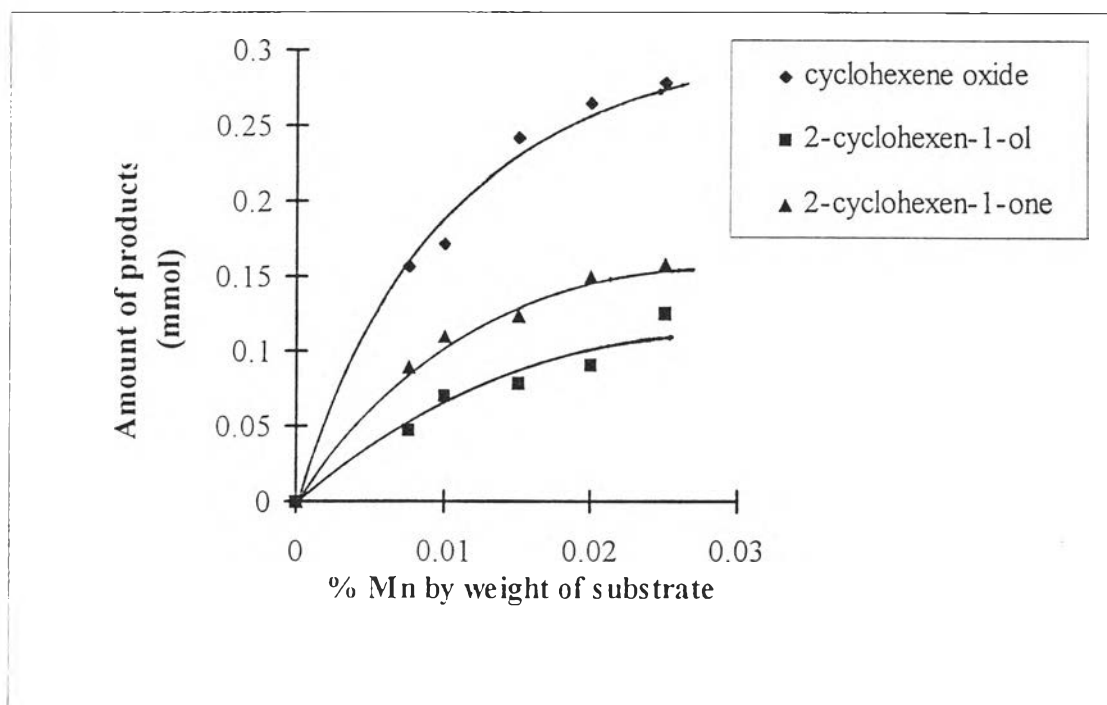
Amount of catalyst (mmol)	Selectivity (%) <sup>a</sup>			Percent conversion <sup>b</sup>	TON <sup>c</sup>
	cyclohexene oxide	2-cyclohexen-1-ol	2-cyclohexen-1-one		
0.0034	53.24	16.04	30.72	1.663	90
0.0045	48.58	20.17	31.25	2.227	80
0.0068	54.40	17.83	27.77	2.506	70
0.0091	52.37	17.98	29.64	2.866	60
0.0114	49.55	22.28	28.16	3.177	50

a) Relative yield of each product to total amount of all oxidation product

b) % Conversion based on formation of oxidation products

c) Turnover number calculated from mmol of products/mmol of MnPcY catalyst

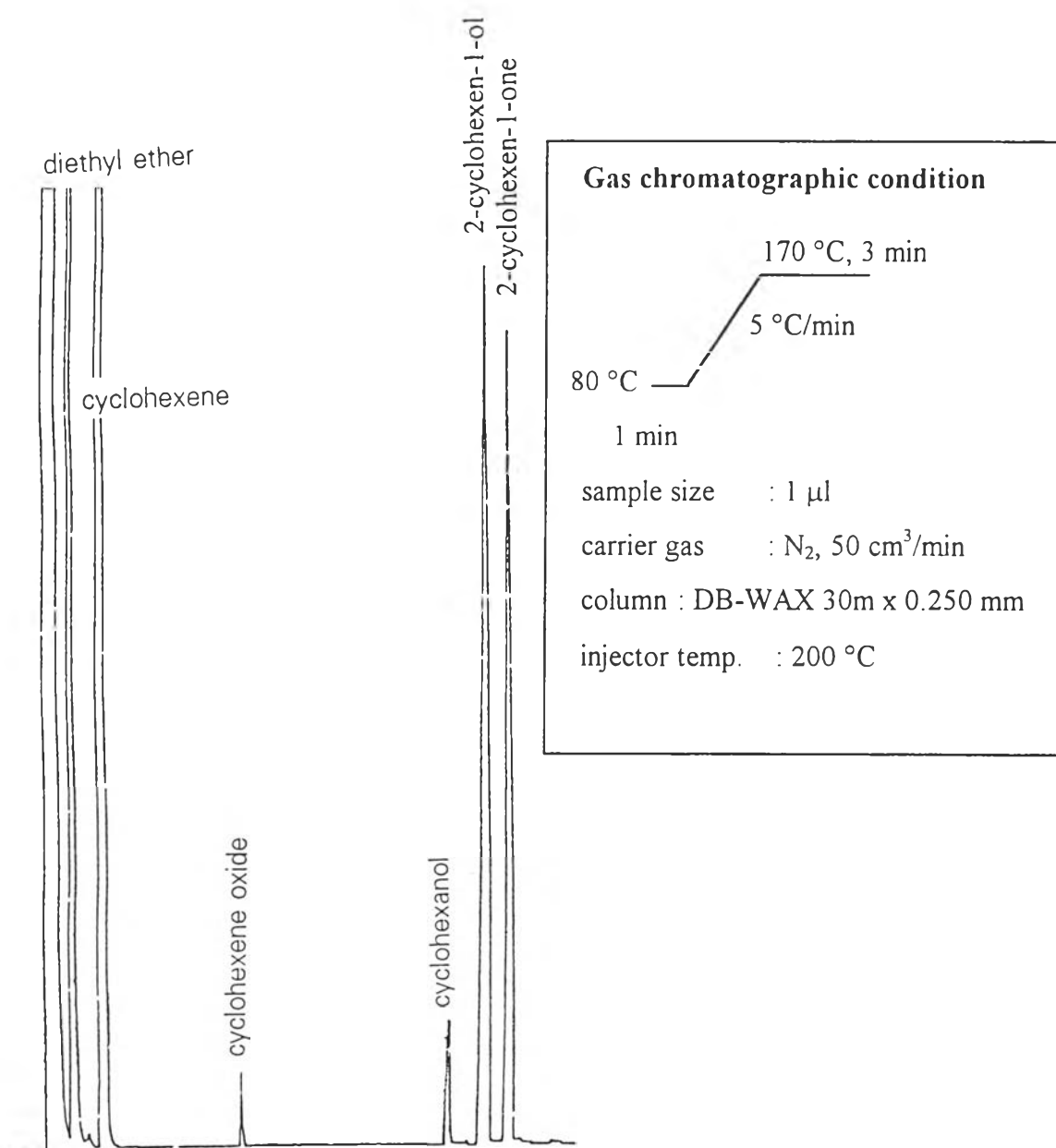
Considering the amount of each oxidation product as shown in Figure 4.15, when the amount of catalyst increases the amount of cyclohexene oxide significantly increases at a higher rate than the other two products. Similar to the results obtained from the previous section, cyclohexene oxide is the major product while 2-cyclohexen-1-ol and 2-cyclohexen-1-one are minor products.



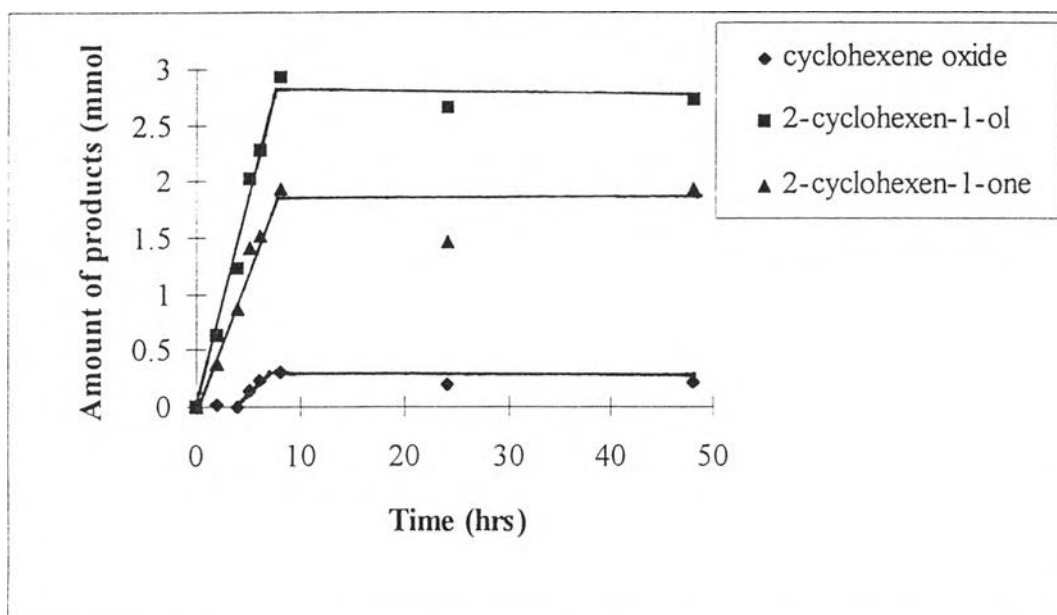
**Figure 4.15** The amount of each product from oxidation of cyclohexene in the absence of solvent using iodosobenzene as oxidant and MnPcY as catalyst

#### 4.4 Catalysis on Oxidation of Cyclohexene Using Oxygen Gas as Oxidant

Another way to improve the catalytic activity is to seek for another type of oxidant which may be appropriate to the system using zeolite entrapped manganese phthalocyanine as catalyst. Hydrogen peroxide and tertiary butyl hydroperoxide were also utilized as oxidants but they were ignored later because they decomposed the zeolite to a gelatinous material. Eventually, replacement of PhIO by oxygen gas as oxidant is intended to get over the problem of stirring. Another reason is to avoid the production of PhI which acts as pore blocking of zeolite and retards substrate to reach the active site of catalyst. The gas chromatogram was shown in Figure 4.16. The catalytic results are shown in Figure 4.17. Similar to the case of oxidation by iodosobenzene, the products are cyclohexene oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one. In contrast to the catalysis using iodosobenzene as oxidant, cyclohexene oxide becomes minor product while 2-cyclohexen-1-ol and 2-cyclohexen-1-one are major products. The result shows that the amount of each product increases rapidly and reaches the saturation point within 8 hours. After 8 hours, there is no change in the amount of products.



**Figure 4.16** Gas chromatogram of liquid phase from oxidation of cyclohexene in the absence of solvent using oxygen gas as oxidant



**Figure 4.17** The amount of each product from oxidation of cyclohexene in the absence of solvent catalyzed by MnPcY using oxygen gas as oxidant

Table 4.5 shows the catalytic activity of MnPcY for oxidation of cyclohexene using oxygen gas as oxidant. This result shows that the system has selectivity to the formation of 2-cyclohexen-1-ol but not cyclohexene oxide. However, 2-cyclohexen-1-one is formed in significant amount but the quantity is less than 2-cyclohexen-1-ol. The turnover number corresponding to the results above shows that the maximum TON can be obtained within 8 hours.

**Table 4.5** Catalytic activity of MnPcY for oxidation cyclohexene without solvent using oxygen gas as oxidant

Time (hrs)	Selectivity (%) <sup>a</sup>			Percent conversion <sup>b</sup>	TON <sup>c</sup>
	cyclohexene oxide	2-cyclohexen- 1-ol	2-cyclohexen- 1-one		
2	1.46	61.13	37.41	3.430	310
4	0.38	58.63	40.99	7.027	620
5	4.02	56.43	39.55	11.927	1060
6	5.75	56.49	37.77	13.460	1190
8	5.83	56.65	37.53	17.223	1520
24	4.69	61.53	33.77	14.400	1280
48	4.28	56.00	39.72	16.190	1430

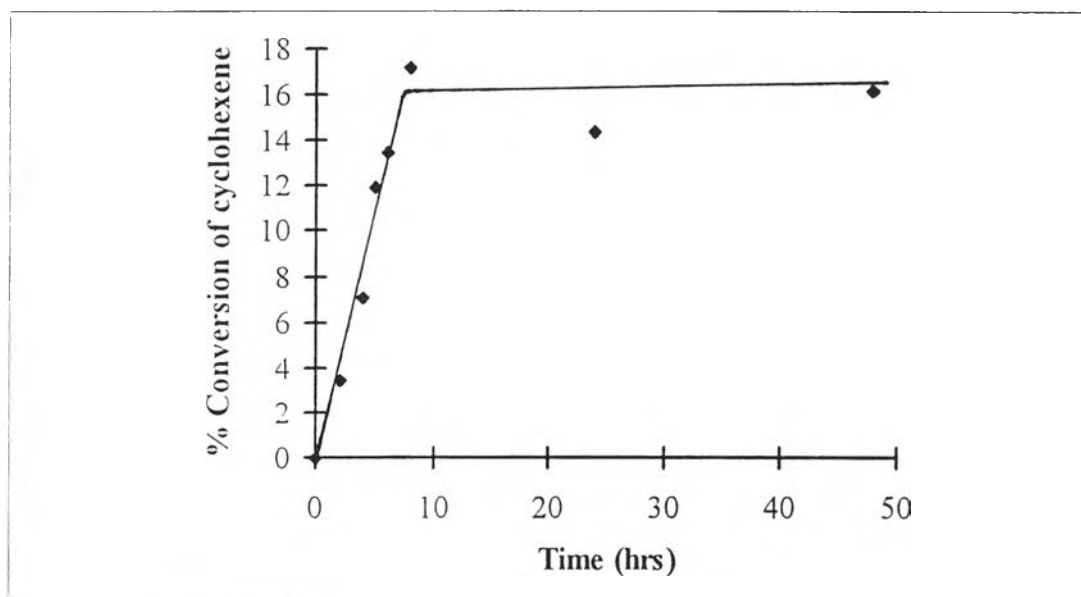
a) Relative yield of each product to total amount of all oxidation product

b) % Conversion based on formation of oxidation products

c) Turnover number calculated from mmol of products/mmol of MnPcY catalyst

Comparing the reaction time for the catalysis using iodosobenzene and oxygen gas, the former takes about three times longer than the latter. This implies that, under the condition utilized in this work, oxygen gas is better oxidant than iodosobenzene. The reason is that oxygen gas can flow through zeolite cavities to reach the active site of the catalyst while the solid iodosobenzene is insoluble. In addition, iodosobenzene is also reduced to phenyl iodide which causes the zeolite pore blocking and retards the substrate to diffuse to the pore of zeolite.

Figure 4.18 shows the time effect on the efficiency on oxidation catalysis of cyclohexene. It is found that % conversion is consistent with the individual profile of formation of products in Figure 4.17. The maximum conversion is obtained within 8 hours.



**Figure 4.18** Percent conversion of cyclohexene catalyzed by MnPcY in the absence of solvent using oxygen gas as oxidant



Table 4.6 shows the catalytic activity of MnPcY catalyst. By increasing the amount of catalyst, there is no effect on the product selectivity. This is different from the system using iodosobenzene as oxidant. It is interesting that the amount of catalyst has strong effect on the % conversion of cyclohexene. By increasing the catalyst amount, the % conversion of cyclohexene can be drastically increased in the system using oxygen as oxidant while there is only little change in the system using PhIO as oxidant as shown in Figure 4.19.

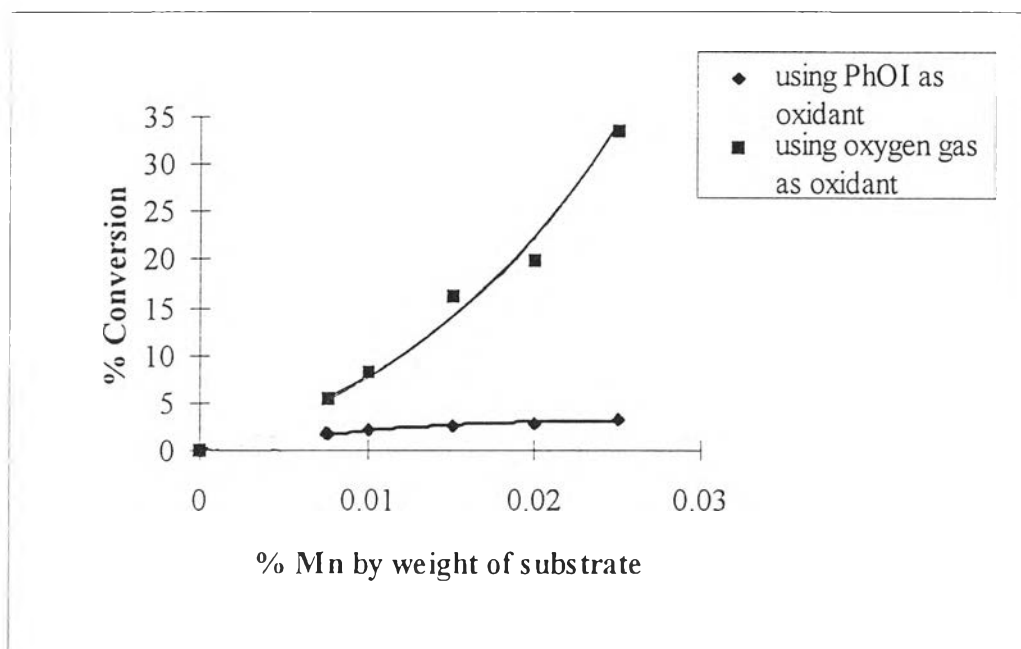
**Table 4.6** Catalytic activity of different amount of MnPcY for oxidation of cyclohexene for 6 hours without solvent using oxygen gas as oxidant

Amount of catalyst (mmol)	Selectivity (%) <sup>a</sup>			Percent conversion <sup>b</sup>	TON <sup>c</sup>
	cyclohexene oxide	2-cyclohexen-1-ol	2-cyclohexen-1-one		
0.0034	2.96	56.08	40.96	5.404	480
0.0045	3.34	58.57	32.80	8.167	550
0.0068	4.11	55.94	39.95	16.227	720
0.0091	4.95	56.19	38.85	19.860	660
0.0114	5.86	56.32	37.82	33.525	890

a) Relative yield of each product to total amount of all oxidation product

b) % Conversion based on formation of oxidation products

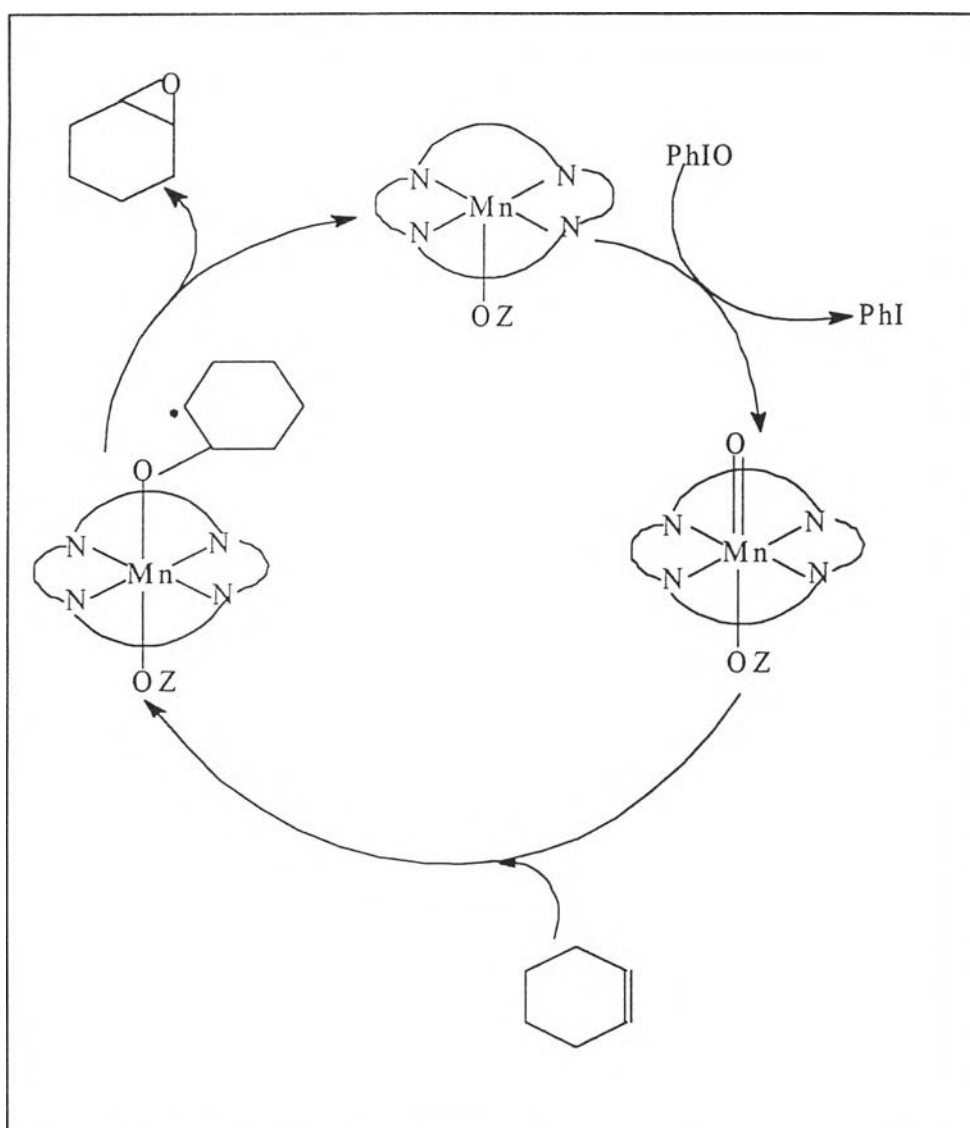
c) Turnover number calculated from mmol of products/mmol of MnPcY catalyst



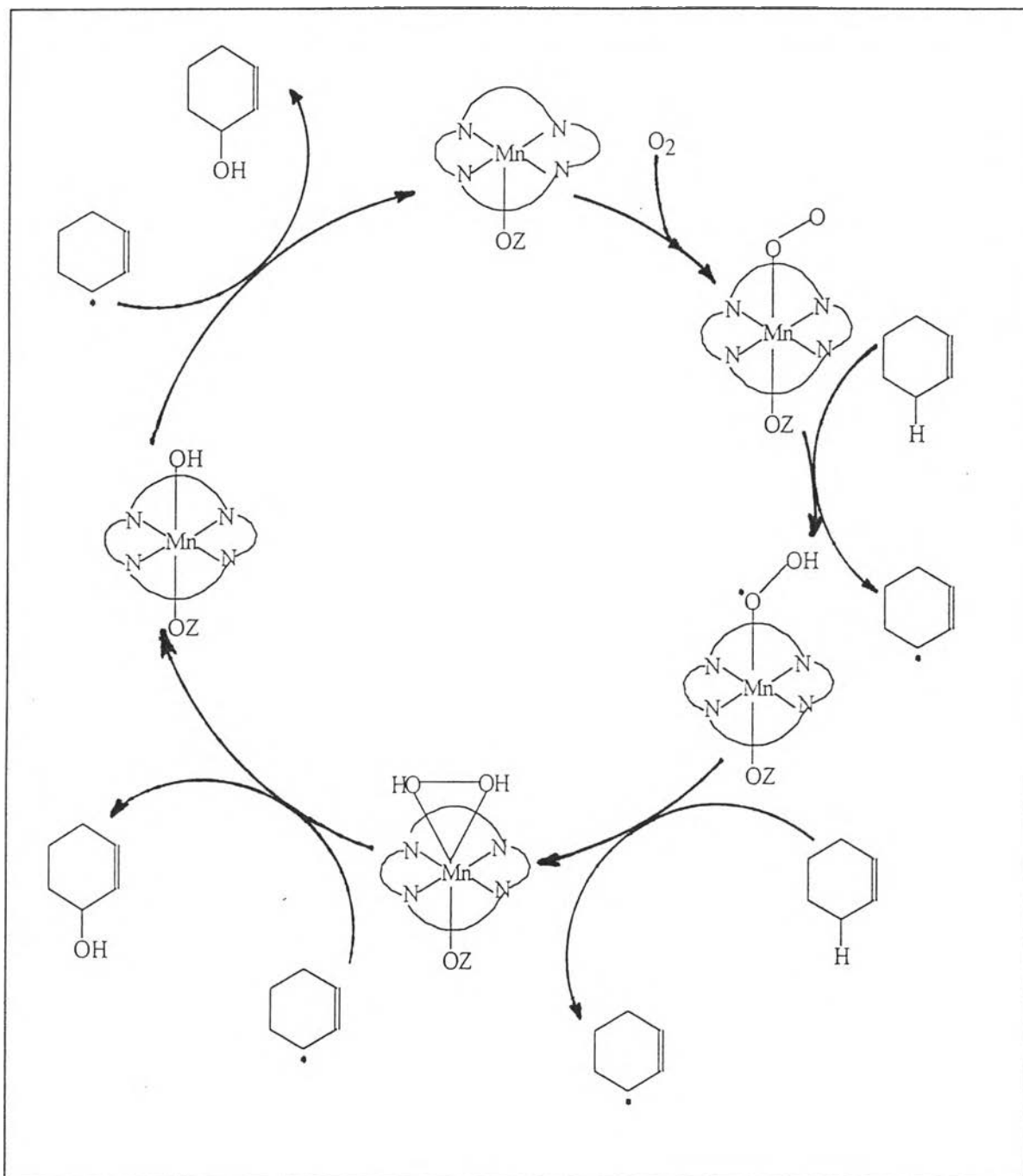
**Figure 4.19** Percent conversion of cyclohexene catalyzed by different amount of MnPcY in the absence of solvent using iodosobenzene and oxygen gas as oxidant

#### 4.5 Proposed Mechanisms for Cyclohexene Oxidation

A mechanism for the catalytic oxidation of cyclohexene to cyclohexene oxide using MnPcY as catalyst and PhIO as oxidant is believed to be similar to that proposed by Groves<sup>59</sup> and Jørgensen<sup>43</sup> for the oxidation system using Mn(TPP)Cl as catalyst. The mechanism is proposed as follows:



For the system using oxygen gas as oxidant, 2-cyclohexen-1-ol is a major product. A possible mechanism is similar to that proposed for the system of hydrocarbon oxidation catalyzed by Cytochrome P450<sup>60</sup> *via* hydrogen abstraction from organic compounds. The mechanism is proposed as follows:



#### 4.6 Oxidation of 1-Hexene

Instead of cyclohexene which is cyclic alkene, 1-hexene which is aliphatic alkene has been utilized as the substrate and PhIO is the oxidant. It is found that the catalyst MnPcY is inactive for oxidation of 1-hexene no matter in the presence or absence of solvent. This is similar to the normal oxidation of alkenes that the reaction is selective to only internal alkene, but not terminal alkene.

If oxygen is used as the oxidant, the catalyst is still inactive for oxidation of 1-hexene although the reaction time is extended up to 72 hours. This result is correspondent to those reported by several researchers<sup>43</sup> that the zeolite loaded macrocyclic compounds are not active for oxidation of terminal alkenes. The difference between 1-hexene and cyclohexene is the shape and size of the substrates. Zeolite Y has unique three dimension pore structure which fits with cyclohexene, not 1-hexene. This is the zeolite property known as shape and size selectivity which is not found in solution system. This may be the reason why cyclohexene can undergo the oxidation catalysis while 1-hexene cannot.

#### 4.7 Conclusion and Suggestions

Zeolite Y (Si/Al = 2.3) was successfully synthesized by the method developed in our laboratory<sup>58</sup>. Slurry of nucleation centers with composition of  $13.5\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 12.5\text{SiO}_2 : 516\text{H}_2\text{O}$  was aged for at least 5 days prior to mixing with the reactant mixture of  $1.9\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 6.0\text{SiO}_2 : 100\text{H}_2\text{O}$ . The obtained milky solution was crystallized at  $100\text{ }^\circ\text{C}$  for 10 - 15 hours. Zeolite MnY was obtained by ion exchange of zeolite NaY with manganese (II) chloride solution.

Zeolite entrapped manganese phthalocyanine was prepared by the process like miniature construction of a ship in the bottle by heating of zeolite MnY and 1,2-dicyanobenzene in vacuum at  $270\text{ }^\circ\text{C}$  for 40 hours. After extraction of crude manganese phthalocyanine with acetone, pyridine and acetone, the manganese phthalocyanine entrapped in zeolite Y which was characterized by IR and UV spectroscopies was obtained. This intrazeolite manganese phthalocyanine complex was stable on heating up to  $200\text{ }^\circ\text{C}$ .

The zeolite entrapped manganese phthalocyanine is the active catalyst for oxidation of cyclohexene using iodosobenzene and oxygen gas as oxidants. The oxidation products identified by GC-MS are cyclohexene oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one. The optimum condition for the system using iodosobenzene as oxidant is 15 mmol cyclohexene,  $3.4 \times 10^{-3}$  mmol MnPcY or 0.015 % Mn by weight of substrate and 7 mmol iodosobenzene in n-octane, with the reaction time of 24 hours. The maximum conversion of this system is 8.067 % with TON of 360 mmol product/mmol catalyst. The catalysis using oxygen gas as oxidant is significantly

improve. The best condition that provides the highest conversion of substrate is the system that using oxygen gas as oxidant and using 30 mmol cyclohexene, 0.0114 mmol MnPcY or 0.025 % Mn by weight and in the absence of solvent with the reaction time of 6 hours. The maximum conversion of this system is 33.5 % with TON of 1470 mmol product/mmol catalyst.

The suggestions for the future work are :

i) Studies of the oxidation of other substrates such as cyclopentene, cyclooctene, and then extended to oxidation of alkane.

ii) The bulkiness of the catalyst that is entrapped in zeolite should be reduced to increase the vacant site in the cavity of zeolite. However, one should be aware of catalyst leaching if the complex is too small, for example, metal-salen complexes.

iii) The transition metal should be fixed in tetrahedral sites in the framework structure of zeolite to prevent the leaching of catalyst.