

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of the Dealuminated Mordenite

4.1.1 Degree of Sodium Exchange by Ammonium Ions

The TOSOH mordenite sample (Si/Al = 11) was ammonium exchanged by three different methods as described in Section 3.4. Samples H-MOR(A), H-MOR(B), and H-MOR(C) were obtained from Methods A, B, and C, respectively. The analysis results of the sodium ions remaining in the dealuminated mordenite, the H-MOR samples are compiled in Table 4.1. The small amount of sodium ions corresponds to the large extent to the sodium ions in Na-MOR that was replaced by exchanging ammonium ions, called degree of ammonium exchange and results in the large amount of hydrogen ions or protons produced after the removal of NH_3 from the NH_4 -MOR samples. From Table 4.1 shows that among the dealuminated mordenite samples obtained from Method C contains the least remained Na^+ ions, or the highest degree of ammonium exchange. Method A results in the only ion exchange in large pores of the mordenite zeolite. For the low content of Na^+ ions remaining in a zeolite the migration of the Na^+ ions from small pores to the large pores is not readily even by several-time repeated ion exchange. However, such a migration can be activated at a high temperature above 500°C before repeated ion exchange. Method C is thus chosen as the optimal method for preparing the dealuminated mordenite samples for the rest of this study.

Table 4.1 Analysis results of the sodium ions remaining in the dealuminated mordenite and the corresponding values of degree of ammonium exchange

Sample	Remained Na Amount	Degree of NH ₄ Exchange
Code	(% by weight)	(%)
Na-MOR	1.09	-
H-MOR(A) ^a	0.74	32
H-MOR(B) ^b	0.38	66
H-MOR(C) ^c	0.09	92

^a H-MOR(A) was prepared by using the ammonium exchange Method A.

^b H-MOR(B) was prepared by using the ammonium exchange Method B.

^c H-MOR(C) was prepared by using the ammonium exchange Method C.

4.1.2 XRD Results

XRD patterns of the H-MOR samples obtained from different methods are shown in Figure 4.1. All three samples, Na-MOR, H-MOR(A) and H-MOR(C) show the characteristic XRD pattern of the mordenite structure without any other phase. H-MOR(B) sample is exchanged in less aggressive condition more than H-MOR(C). Therefore, the H-MOR(B) should have intact XRD pattern resulted, and structure as its H-MOR(C). This indicates that the mordenite structure is very stable and intact by any ion exchange process.

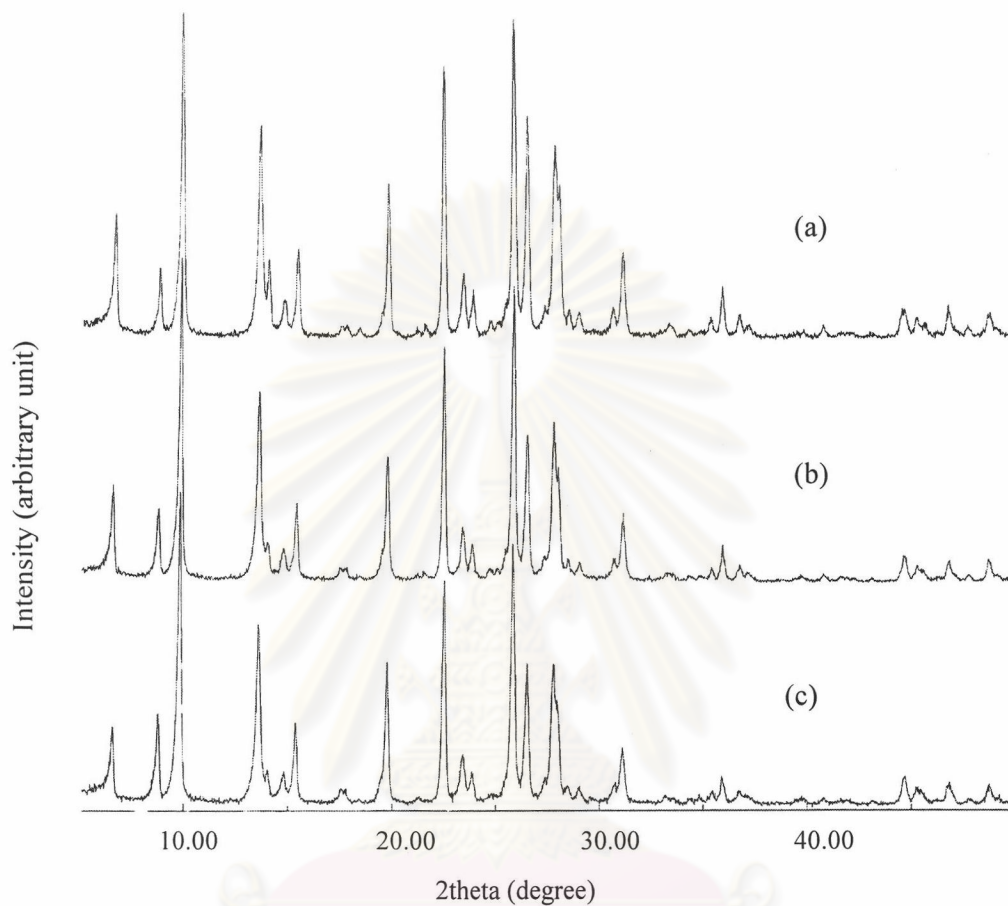


Figure 4.1 XRD patterns of the H-MOR samples corresponding to those in Table 4.1, (a) Na-MOR, (b) H-MOR(A) and (c) H-MOR(C).

4.2 Factors Involved in Dealumination of Mordenite

4.2.1 Effect of Temperature on Dealumination of Mordenite

After the treatment of the H-MOR(C) sample with the HCl solution of 1 M for 3 h at various temperatures, some aluminum contents were removed from the mordenite sample depending on the temperatures. The result of chemical analysis for aluminum contents

in the dealuminated mordenite samples was shown in Table 4.2. The Si/Al molar ratios in the samples increase with increasing temperatures. However, the aluminum contents remaining in the treated samples are not much different.

Table 4.2 The Si/Al ratios in the mordenite zeolite treated with the HCl solution of 1 M for 3 h at various temperatures

Temperature (°C)	Si/Al ratio
90	24
100	30
110	33
120	36

Figure 4.2 shows the results of temperature programmed desorption of ammonia (NH₃-TPD) for H-MOR treated with the HCl solution of 1 M for 3 h at various temperatures, 90, 100, 110, and 120°C. All NH₃-TPD profiles exhibit two types of acid sites in the treated H-MOR samples. They are generally assigned³⁸⁻³⁹ to weaker acid sites (the desorbed ammonia peak at lower temperature with a maximum at 180°C) due to Brønsted acidity and stronger acid sites (the desorbed ammonia peak at higher temperature with a maximum at 430°C) due to Lewis acidity. Similar to other reports,³⁸ increasing temperature for the acid treatment results in the decrease of the number of Lewis acid sites. This indicates that the lowering of the number of Lewis acid sites is directly proportional to the aluminum content remained in H-MOR. Usually, an Al atom in the zeolite framework is a four-coordination center bound to bridging oxygen atoms and thus the tetrahedral AlO₄⁵⁻ or

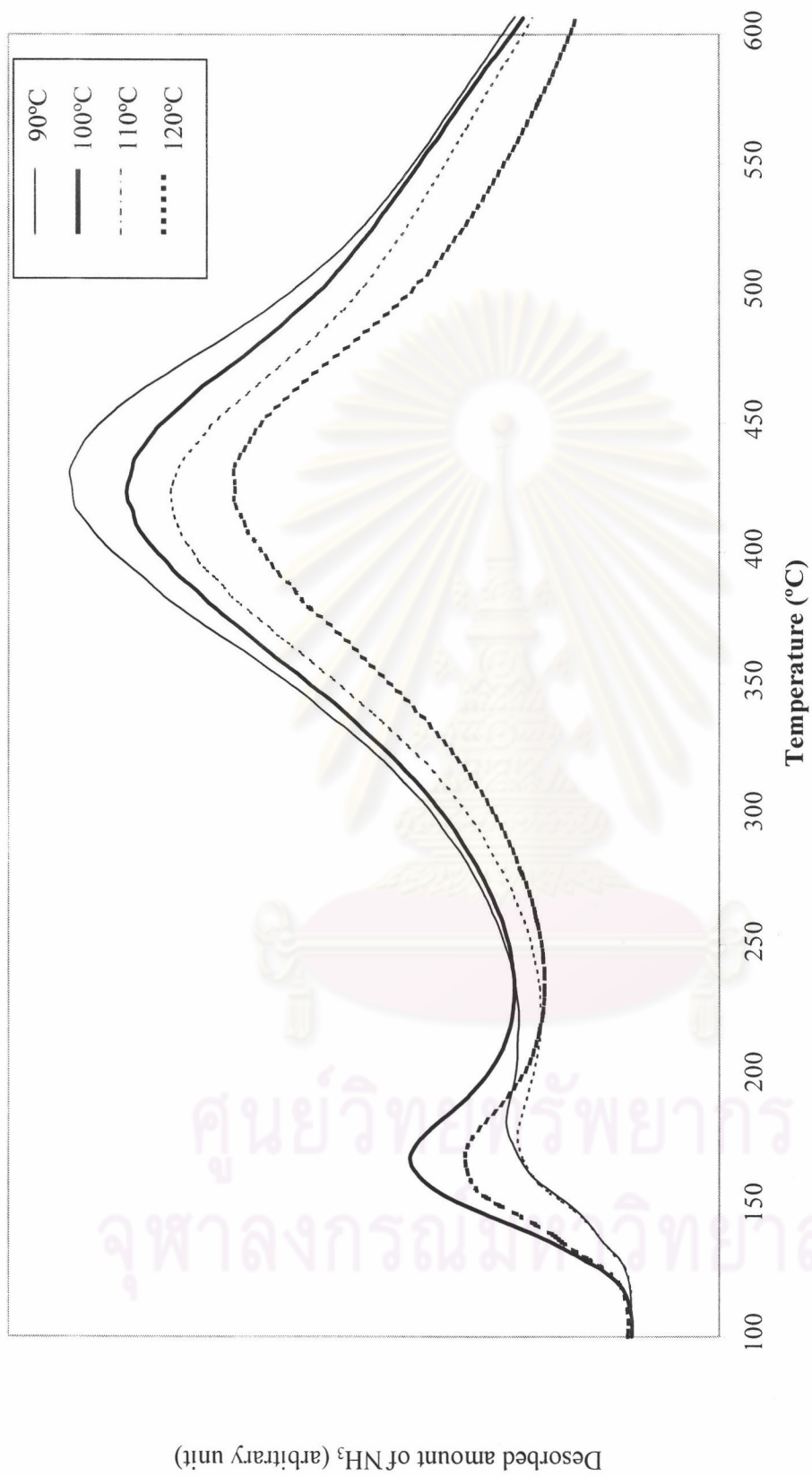


Figure 4.2 NH_3 -TPD profiles of H-MOR treated by 1.0 M hydrochloric acid at 90, 100, 110 and 120 $^{\circ}\text{C}$ for 3 h.

empirically AlO_2^- needs a cation (H^+) to balance the negative charge. This is known as the Brønsted acid site. The four-coordinated aluminum can transfer reversibly to a three-coordination type that is electron deficient and accounted for Lewis acid sites. However, in the case of low aluminum content or high Si/Al ratio, the Lewis acid is predominant to Brønsted acid and plays an important role on acid catalytic activity of the zeolite.

4.2.2 Effect of Acid Concentration on Dealumination of Mordenite

The Si/Al ratios in the dealuminated H-MOR obtained from the acid leaching at 100°C using HCl of various concentrations between 0.1 and 6.0 M are shown in Table 4.3 and Scheme 4.1.

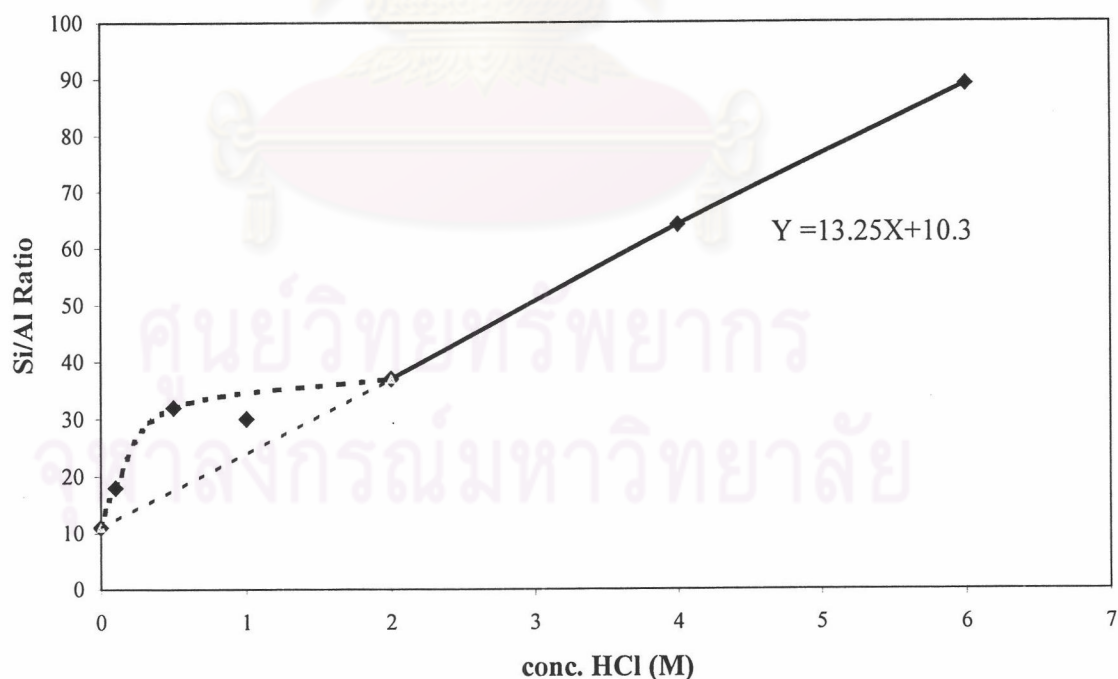
Table 4.3 The Si/Al ratios in the mordenite zeolite treated with the HCl solution of various concentrations at 100°C for 3 h

HCl Concentration (M)	Si/Al ratio
0	11
0.1	18
0.5	32
1.0	30
2.0	38
4.0	64
6.0	89

Increasing the concentration of the HCl solution causes obviously the increase in the Si/Al ratios in the product. The Si/Al ratios in the dealuminated H-MOR is in linear proportional to the HCl concentrations within a range of 2.0-6.0 M. A linear equation is represented by

$$Y = 13.25X + 10.5$$

where Y is the Si/Al ratio and X is the HCl concentration. However, one should notice that at the HCl concentration below 2.0 M the relation between the Si/Al ratios and the HCl concentrations deviates from the linear line and has a behavior as a dashed curve shown in Scheme 4.1. This indicates that if an extrapolation of the linear line is used, a mistake will be made. The H-MOR samples with low Si/Al ratios shall be prepared by direct synthesis rather than the post-synthesis by dealumination.



Scheme 4.1 A relation between the Si/Al ratios in the dealuminated mordenite and the HCl concentrations in the treatments at 100°C for 3 h.

XRD patterns of the H-MOR samples treated with the HCl solutions of 4 and 6 M were measured to ensure that the MOR structure is not affected by the mineral acid treatment. The XRD results shown in Figure 4.3.

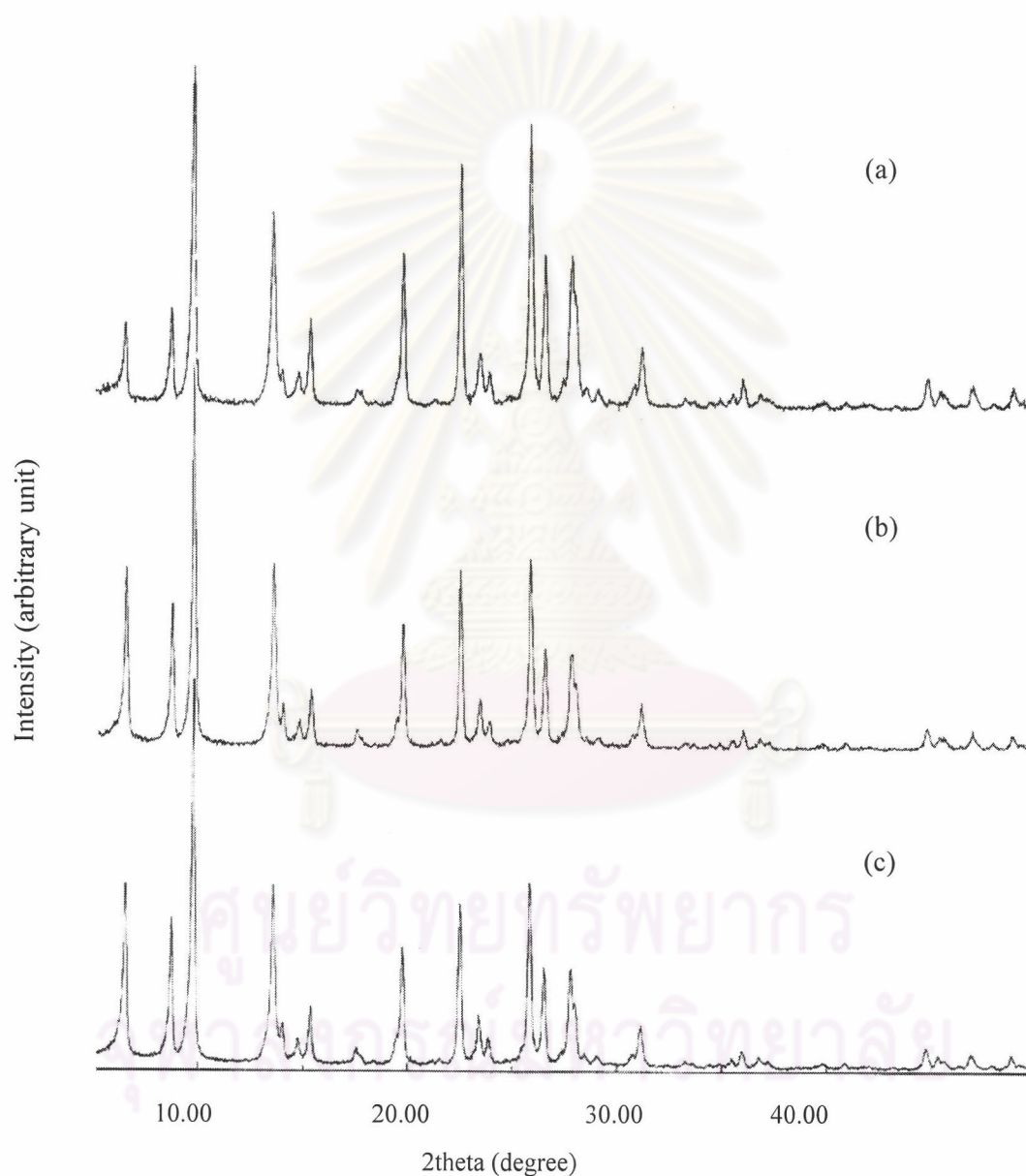


Figure 4.3 XRD patterns of the H-MOR samples, (a) untreated H-MOR with Si/Al = 11, (b) the H-MOR treated with 4.0 M of HCl at 100°C for 3 h, and (c) H-MOR treated with 6.0 M of HCl at 100°C for 3 h.

The XRD results have proven that the MOR structure is not affected by the strong acid treatment. Therefore, to obtain a dealuminated H-MOR with a required Si/Al ratio, the HCl concentration can be calculated from the equation described above. For example, the H-MOR with Si/Al ratio of 20, 40 and 80 may be prepared by using the HCl solution of 0.1, 2.3 M and 5.5 M, respectively.

The ^{27}Al -NMR spectrum of the dealuminated H-MOR (Si/Al = 39) was shown in Figure 4.4. The most predominant peak at a chemical shift of 56 ppm belongs to the tetrahedral aluminum atoms in the framework structure of H-MOR.³⁹⁻⁴¹ There is only a little signal of the octahedral aluminum atoms of which a chemical shift is 0 ppm, located on the surface of the H-MOR but at the framework position. The peak height of the framework Al and non-framework Al is 8:1. This indicates that the amount of the framework Al is 90 % and 10 % for the non-framework Al.

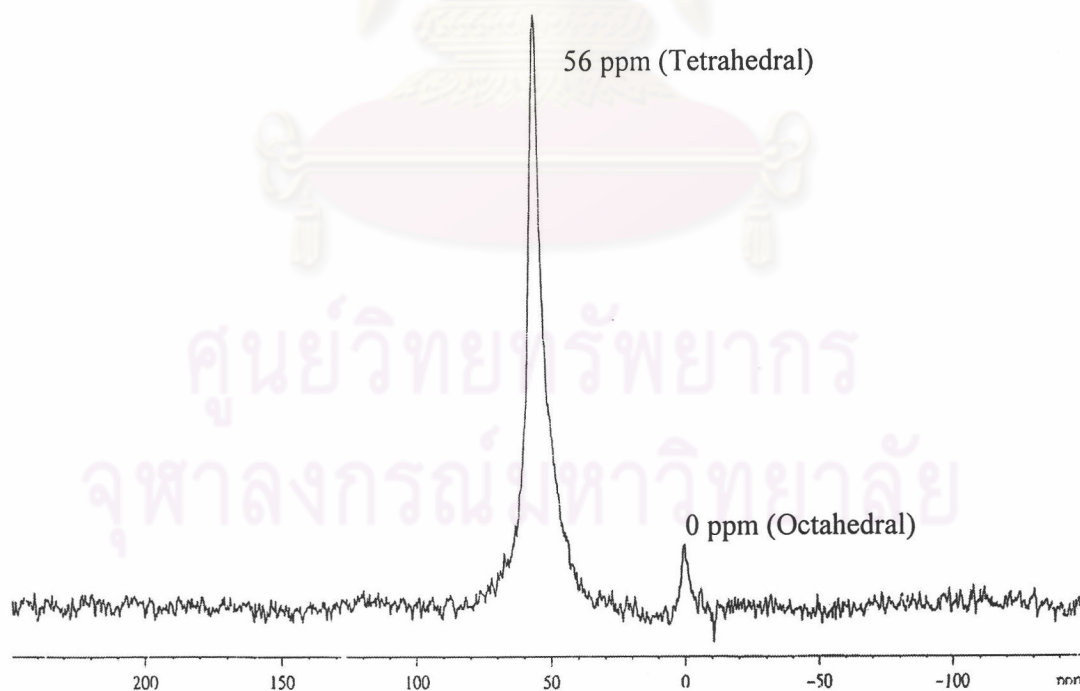


Figure 4.4 The ^{27}Al -NMR spectrum of the dealuminated H-MOR (Si/Al = 39) prepared by the acid leaching using a HCl solution of 2.3 M at 100°C for 3 h.

4.3 The Dealuminated Mordenite Catalysts

The Na-MOR catalyst with the Si/Al ratio of 11 was dealuminated by hydrochloric acid solution with the concentration of 0.1, 2.3 and 5.5 M. XRD patterns of those samples are shown in Figure 4.5. All samples have intact structure of mordenite. In addition, they were analyzed for the Si/Al ratio in catalysts by ICP-AES and the results are shown in Table 4.4.

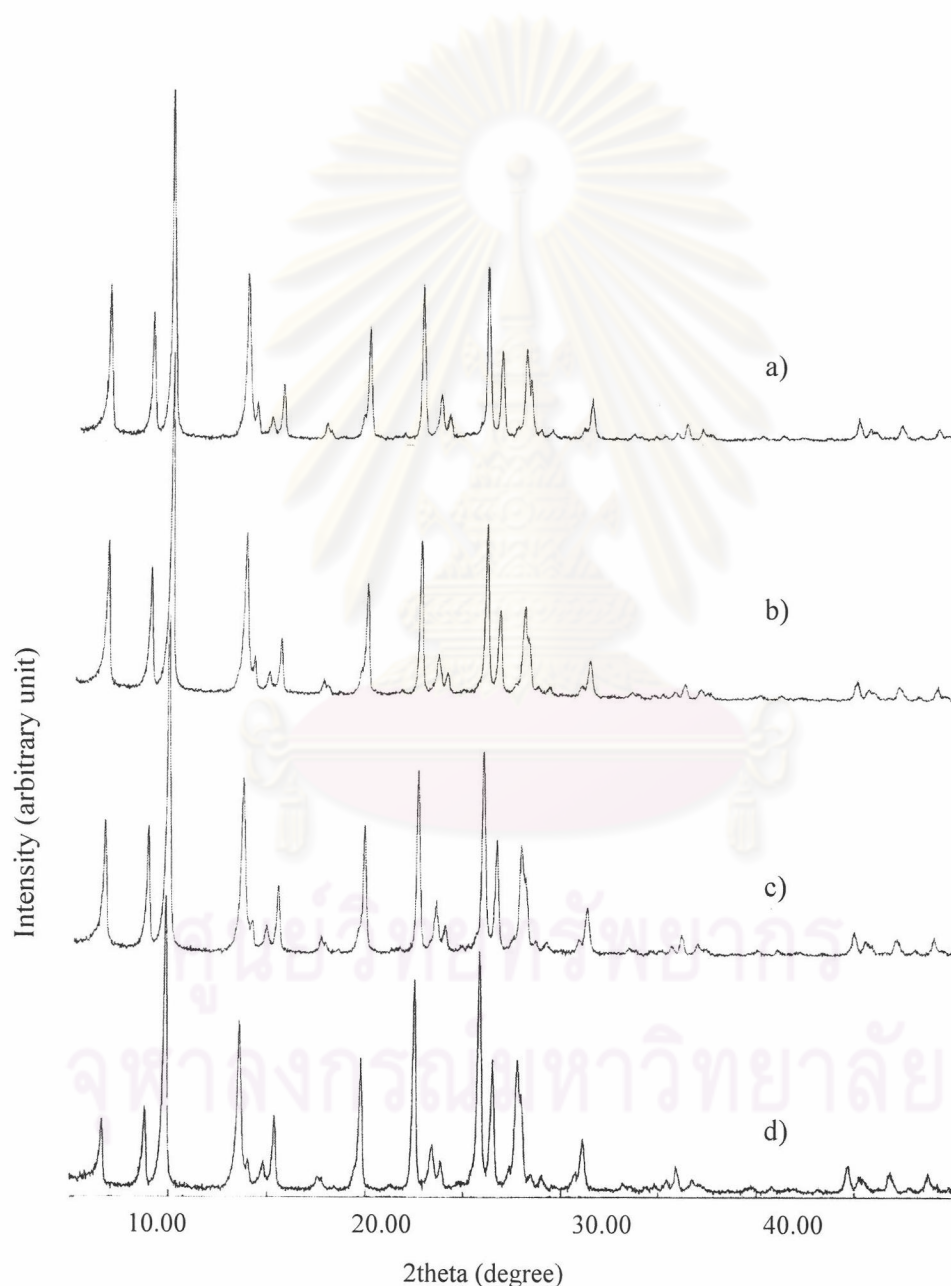


Figure 4.5 XRD patterns of the H-MOR samples, a) untreated H-MOR with Si/Al = 127, b) treated with 5.5 M of HCl at 100°C for 3 h, c) H-MOR treated with 2.3 M of HCl at 100°C for 3 h, and d) untreated H-MOR with Si/Al = 11.

Table 4.4 Analysis results of the Si/Al ratio in catalysts by ICP-AES

Concentration of HCl solution (M)	Remaining Al Amount (% by weight)	Si/Al ratio
0.1	4.29	19
2.3	1.78	47
5.5	0.93	90

4.4 Catalytic Activity of Mordenite in Polypropylene Degradation

4.4.1 Polypropylene Degradation over H-MOR with Various Si/Al Ratios

Values of conversion and product yield obtained from polypropylene degradation over H-MOR with various Si/Al ratios at the temperature of 450°C are shown in Table 4.5. From Table 4.5, %conversions are as high as about 100% for all Si/Al ratios in catalyst and coke formation is at about 10-12%wt of catalyst. Formation of gas products and liquid products as well as coke is not affected by different Si/Al ratios in catalyst.

Product distributions in gas phase are shown in Figure 4.6. At lower Si/Al ratio, or high aluminum content, four types of products are formed in a significant amount. They are propane, propylene, *iso*-butane and *iso*-butene. The product distribution is affected by a variation in Si/Al ratio in catalyst. With increasing the Si/Al ratio, or reducing aluminum content, the selectivity to propylene increases from 19.1 to maximum at 30% at the Si/Al ratio of 127 in catalyst. At the same time, catalyst with high Si/Al ratio can inhibit formation of propane. It is interesting that methane formation is very rare at the Si/Al ranged from 19 to 127. This is an advantage of zeolite catalysts over non-zeolite catalysts that often provide significant amount of methane at a high value of conversion.

Table 4.5 Values of conversion and product yield obtained from polypropylene degradation over H-MOR with various Si/Al ratios at the temperature of 450°C

	Catalyst				
	H-MOR(11)	H-MOR(20)	H-MOR(50)	H-MOR(90)	H-MOR(120)
Si/Al in catalyst	11	19	47	90	127
Al ₂ O ₃ content (% wt)	7.6	4.3	1.8	0.9	0.7
Conversion of propylene (%)	99	100	99	99	98
Yield of gas fraction (% wt)	68	71	72	72	71
Yield of volatile liquid fraction (% wt)	7.1	5.0	8.3	3.7	1.2
Yield of non-volatile liquid fraction (% wt)	20	19	14	20	20
Coke (% wt of catalyst)	9.8	10	10	10	12

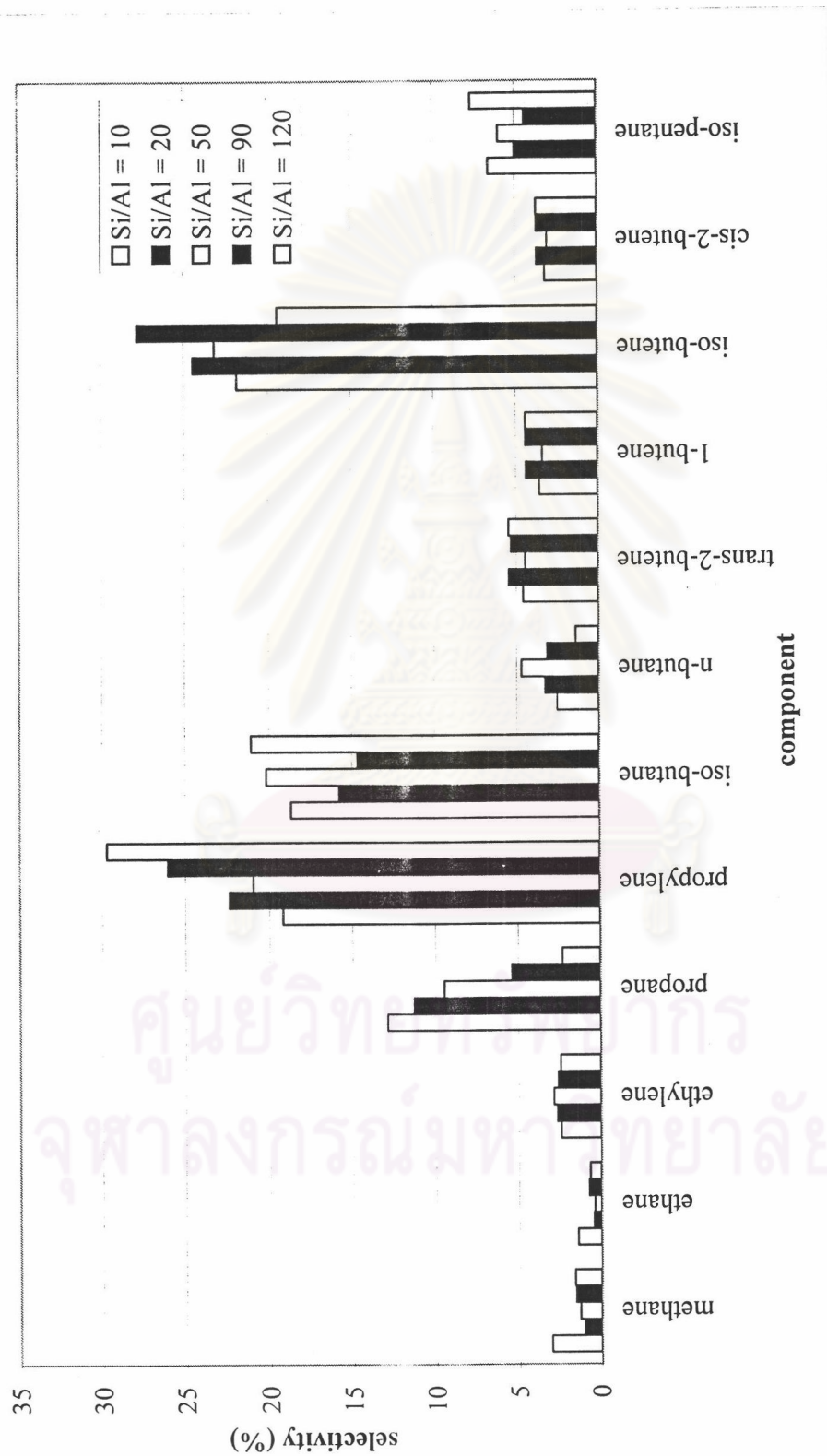


Figure 4.6 Product distributions in gas phase for polypropylene degradation using the mordenite catalysts with various Si/Al ratios at the temperature of 450°C.

Product distributions in volatile liquid obtained from the catalytic degradation of polypropylene over the H-MOR catalyst with various Si/Al ratios are shown in Figure 4.7. Each hydrocarbon was identified by a number of carbon atoms in a molecule including its isomers, for example, C₉+ where C₉ represents for a combination of aliphatic molecules containing nine carbon atoms and the positive sign is noted for other products larger than C₉. The data show that the liquid fraction covers a broad range of hydrocarbons. Aromatic fraction consists of benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene etc. The C₉+ fraction is formed with the most selectivity in volatile liquid products at each Si/Al ratio. With increasing Si/Al ratios in catalyst, the selectivity to C₉+ and aromatics change in the opposite direction to values of selectivity to C₅ and C₆ fractions. Cracking C₉+ and aromatics fraction results in formation of C₅ and C₆ fractions. It seems that the selectivity is not consistent with the change in Si/Al ratio in catalyst. The effect of Si/Al ratio in catalyst is not clear enough, therefore more data in future work are needed to make discussion in detail.

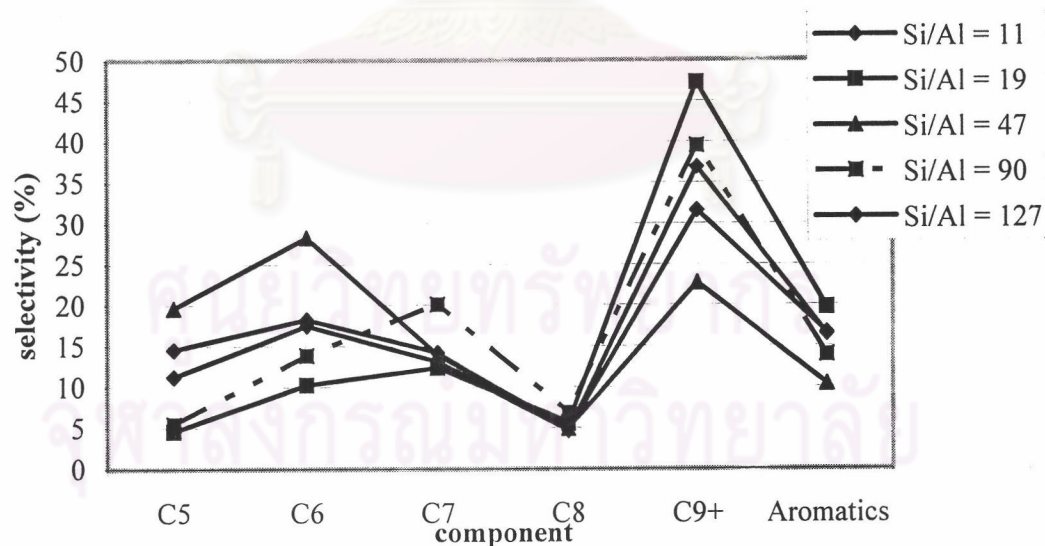


Figure 4.7 Product distributions in volatile liquid obtained from the catalytic degradation of polypropylene over the H-MOR catalysts with various Si/Al ratios at the temperature of 450°C.

The mordenite catalyst with the Si/Al of 127 gives propylene the most among other catalysts. Hence, it is used in polypropylene degradation at various temperatures.

4.4.2 Polypropylene Degradation at Various Temperatures

Values of conversion and product yield obtained from polypropylene degradation over H-MOR with the Si/Al ratio of 127 at various temperatures are shown in Table 4.6. From Table 4.6, values of conversion and product yield are significantly affected by temperature. With increasing temperature from 350 to 450 and 550°C, conversion of polypropylene increases from 90 to 98 and 98%, respectively. This indicates that temperature has strong effect on conversion only at the temperature ranged from 350 to 450°C. There is no difference in conversion beyond the temperature. It is a drastic change in coke formation as well. The amount of coke formed in the catalysts was as huge as 76% at 350°C but drastically decreases to 13 and 15% at the temperature of 450 and 550°C, respectively.

Table 4.6 Values of conversion and product yield obtained from polypropylene degradation over H-MOR with the Si/Al ratio of 127 at various temperatures

	Temperature (°C)		
	350	450	550
Conversion of propylene (%)	90	98	98
Yield of gas fraction (% wt)	34	71	79
Yield of volatile liquid fraction (% wt)	26	20	12
Yield of non-volatile liquid fraction (% wt)	7.6	1.2	0.1
Coke (% wt of catalyst)	76	13	15

In addition the significant change in yields of gas products and liquid products are also found between 350 and 450°C rather than between 450 and 550°C. It is observed that the yield of gas is inversely related to the coke content. However, both are not consistent with the yield of liquid products.

Product distributions in gas phase fraction obtained from the catalytic degradation of polypropylene over the H-MOR catalyst with various temperatures are shown in Figure 4.8. With increasing temperature from 350 to 450°C, selectivity to propylene significantly increases from 18 to 30%, and selectivity to *iso*-butene slightly change from 17 to 19%. Selectivity to *iso*-butane decreases from 28 to 23% and selectivity to methane drastically decreases from 5.6 to 1.6%. From Figure 4.8 all gas components are almost unchanged in selectivity by further increasing temperature to 550°C. It can be concluded that the temperature of 450°C is optimal for polypropylene degradation over the H-MOR(127) catalyst to give the highest selectivity to propylene and the lowest selectivity to other gaseous product is 450°C.

Product distributions in volatile liquid fraction obtained from the catalytic degradation of polypropylene over the H-MOR catalyst with various temperatures are shown in Figure 4.9. The data show that the liquid fraction covers a broad range of hydrocarbons. With increasing temperature, selectivities to aromatics and C₉+ fractions increase while selectivities to other smaller products of C₅ to C₈ decrease. This is accounted by the kinetic effect. At high temperatures the small cracking products having high kinetic energy may collide to each other and readily form oligomers ranged in C₉+ fraction.

The data at various temperatures indicate that catalytic cracking of polypropylene takes place readily even at 350°C but with high content of coke in the catalyst. This is accounted by the strong acidity of mordenite similar to other zeolite catalysts. Running the catalytic cracking of polypropylene at the temperature of 450°C can diminish coke amount. It appears that degraded polypropylene can access to active acid sites located in large pore of 12-member ring in mordenite rather than in small pore of 8-member ring. The reason

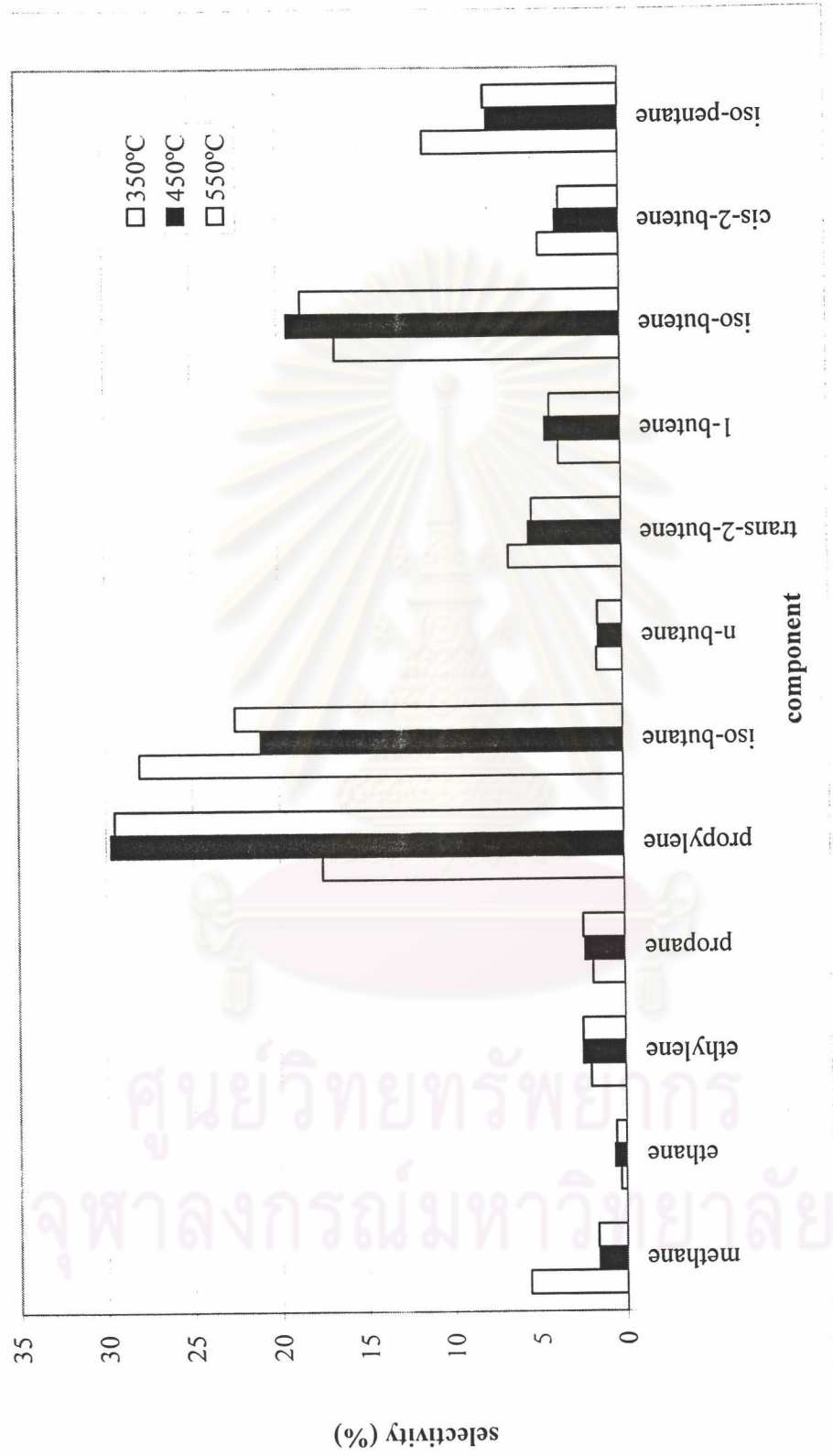


Figure 4.8 Product distributions in gas phase fraction obtained from the catalytic degradation of polypropylene over the H-MOR(127) catalyst with various temperatures.

is the polypropylene degradation is not favored in ZSM-5 owing to limited diffusion through a medium pore 10-member ring.^{17-19,22} This is an advantage of large pore zeolite like mordenite over smaller pore zeolite such as ZSM-5.

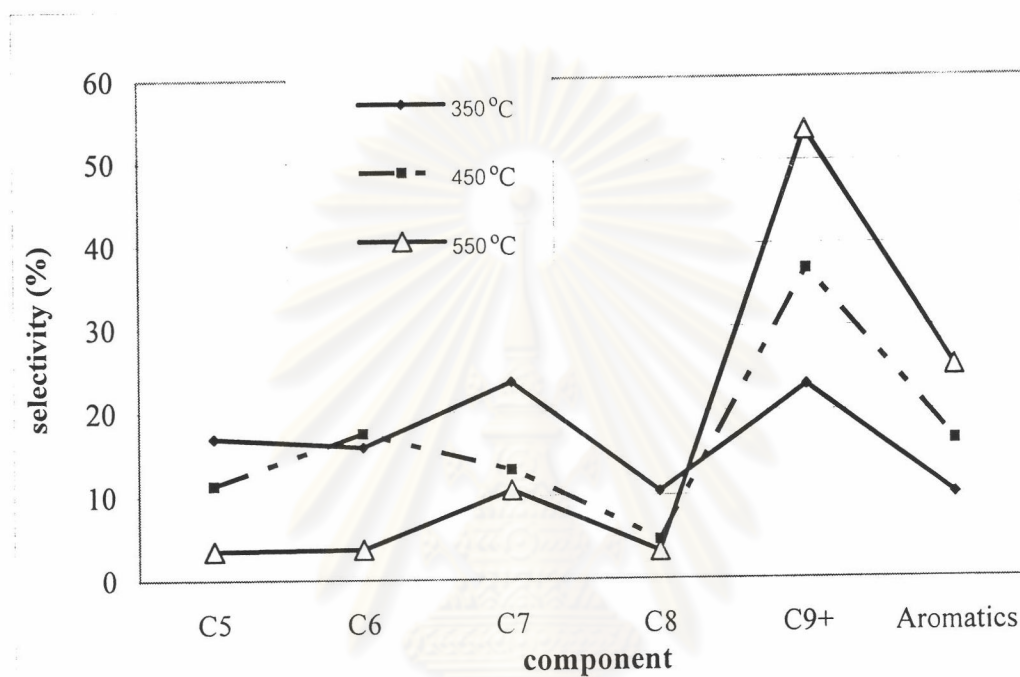


Figure 4.9 Product distributions in volatile liquid obtained from the catalytic degradation of polypropylene over the H-MOR(127) catalyst with various temperatures.

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4.5 Catalytic Activity of Mordenite in Polyethylene Degradation

4.5.1 Polyethylene Degradation over H-MOR with Various Si/Al Ratios

Values of conversion and product yield obtained from polypropylene degradation over H-MOR with various Si/Al ratios at the temperature of 450°C are shown in Table 4.7. Similarly to degradation of polypropylene, conversion and product yield obtained for polyethylene degradation are not different. All catalysts give very high activity of 98-99% conversion of polyethylene and coke formation is at about 10-15%wt of catalysts. There is no doubt for high activity of the mordenite catalyst in polyethylene degradation because its degraded polymer is relatively smaller than that of polypropylene. Thus there is enough space for the degradation can take place.

Product distributions in gas phase are shown in Figure 4.10. At lower Si/Al ratio, or high aluminum content, four types of products are formed significantly (more than 10mol%). They are propane, propylene, *iso*-butane and *iso*-butene. With increasing Si/Al ratio in catalyst, selectivity to propylene tends to decrease except for the Si/Al of 127 that it jumps to the highest selectivity. For *iso*-butene, its selectivity decreases with increasing Si/Al from 11 to 127. In contrast, the composition of *iso*-butane increases. Propane composition seems unaffected except for the Si/Al ratio of 127, it decreases to about one half.

In volatile liquid fraction C₉+ is a major product for all Si/Al ratios in catalyst as shown in Figure 4.11. Compositions of C₉+ and aromatics have the highest selectivity when the H-MOR catalyst with the Si/Al of 127 was used as catalyst. However, the selectivity to each liquid product does not correspond to Si/Al ratios in catalyst.

Table 4.7 Values of conversion and product yield obtained from polyethylene degradation over H-MOR with various Si/Al ratios at the temperature of 450°C

	Catalyst				
	H-MOR(11)	H-MOR(20)	H-MOR(50)	H-MOR(90)	H-MOR(120)
Si/Al in catalyst	11	19	47	90	127
Al ₂ O ₃ content (% wt)	7.6	4.3	1.8	0.9	0.7
Conversion of ethylene (%)	99	98	99	98	98
Yield of gas fraction (% wt)	79	71	68	66	62
Yield of volatile liquid fraction (% wt)	14	20	22	19	20
Yield of non-volatile liquid fraction (% wt)	0.4	2.1	5.0	8.0	11
Coke (% wt of catalyst)	13	12	10	10	15

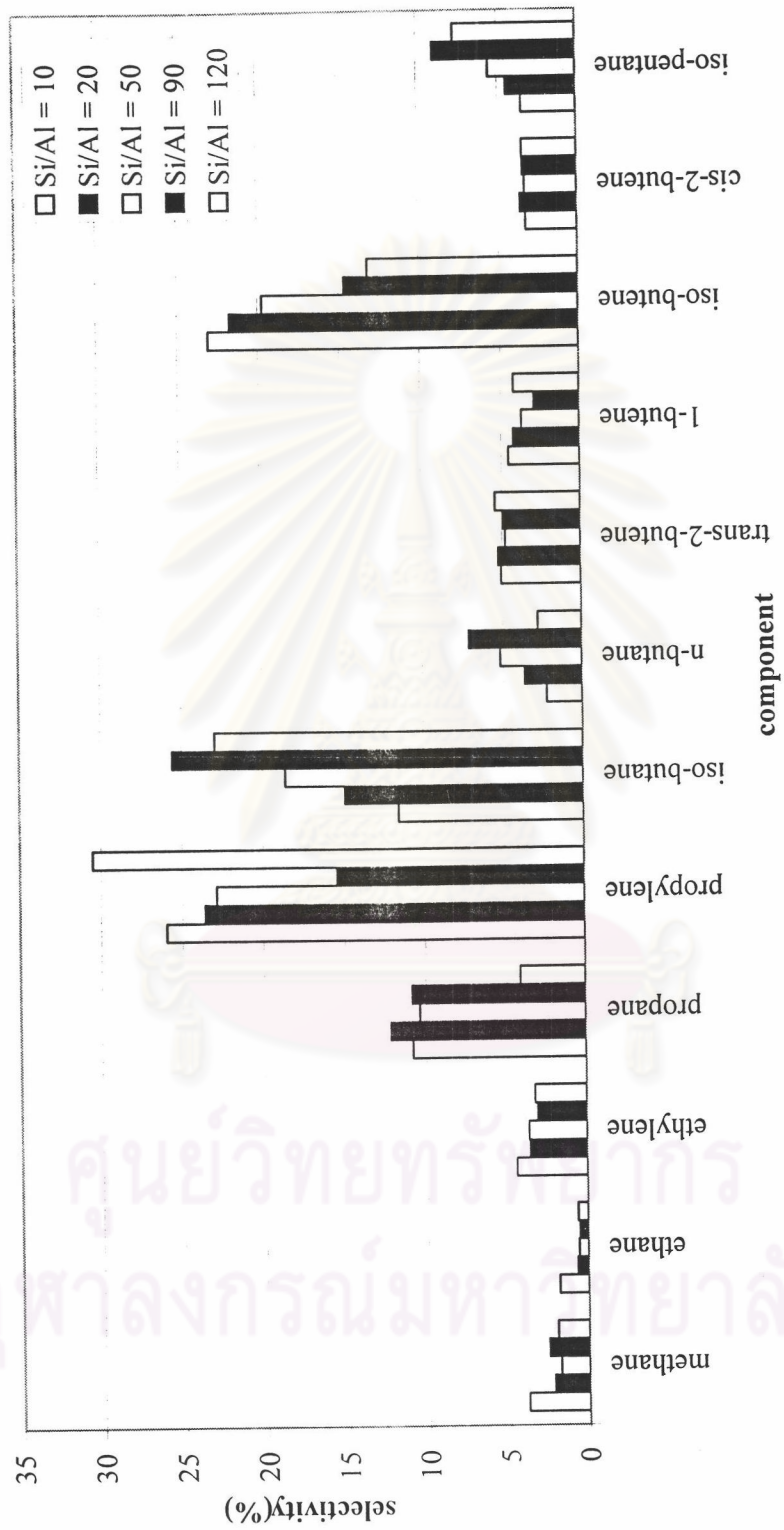


Figure 4.10 Product distributions in gas phase for polyethylene degradation using the mordenite catalysts with various Si/Al ratios at the temperature of 450°C.

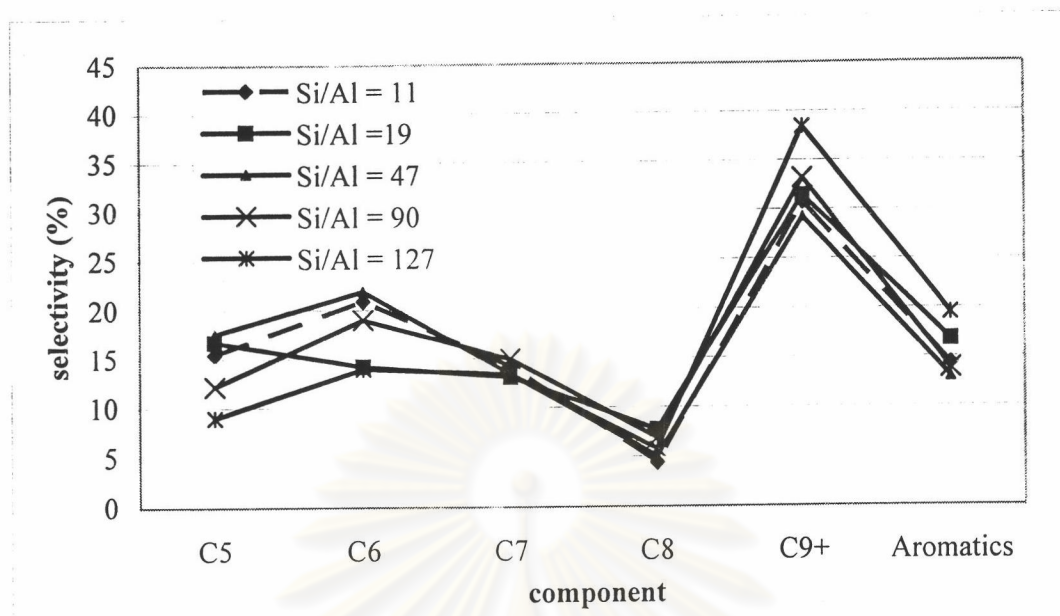


Figure 4.11 Product distributions in volatile liquid obtained from the catalytic degradation of polyethylene over the H-MOR catalysts with various Si/Al ratios at the temperature of 450°C.

The mordenite catalyst with the Si/Al of 127 gives propylene the most among other catalysts. Hence, it is used in polyethylene degradation at various temperatures.

4.5.2 Polyethylene Degradation at Various Temperatures

Conversions and product yields obtained from polyethylene degradation at various temperatures are shown in Table 4.8. The results are in similar trends as observed for polypropylene cracking. From Table 4.8, with increasing temperature from 350 to 450°C, the value of conversion is changed from 85% to 98%. Conversions at temperatures of 450 and 550°C are not different. Coke is formed at high amount of 90% at 350°C and drops to 14% at the temperature of both 450 and 550°C. Yield of Gas products increases from 26 to 62 and 76% with the increase in temperature. Liquid fraction is formed in similar yield at 350 and 450°C. It reduces to only one half at the temperature of 550°C.

Table 4.8 Values of conversion and product yield obtained from polyethylene degradation over H-MOR with the Si/Al ratio of 127 at various temperatures

	Temperature (°C)		
	350	450	550
Conversion of ethylene (%)	85	98	98
Yield of gas fraction (% wt)	26	62	76
Yield of volatile liquid fraction (% wt)	23	20	13
Yield of non-volatile liquid fraction (% wt)	11	11	4
Coke (% wt of catalyst)	90	15	14

Product distributions in gas phase obtained from polyethylene degradation at various temperatures are shown in Figure 4.12. At the temperature of 350°C, gas composition is 17% methane, 1.5% ethylene, 13% propylene, 16% *iso*-butane, 10% *trans*-butene, 16% *iso*-butene, and 9% *iso*-pentane. With increasing temperature, methane, and butenes decrease while the rest increase. At 450°C propylene has highest selectivity of 31%, *iso*-butane has selectivity of 23, ethylene has selectivity of 3.2% and methane has selectivity of 2%. Instead of ethylene, propylene is a major product from polyethylene degradation. This may be the shape selectivity of large pore zeolite to form propylene but medium pore zeolite like ZSM-5 is selective to form ethylene from polyethylene cracking.

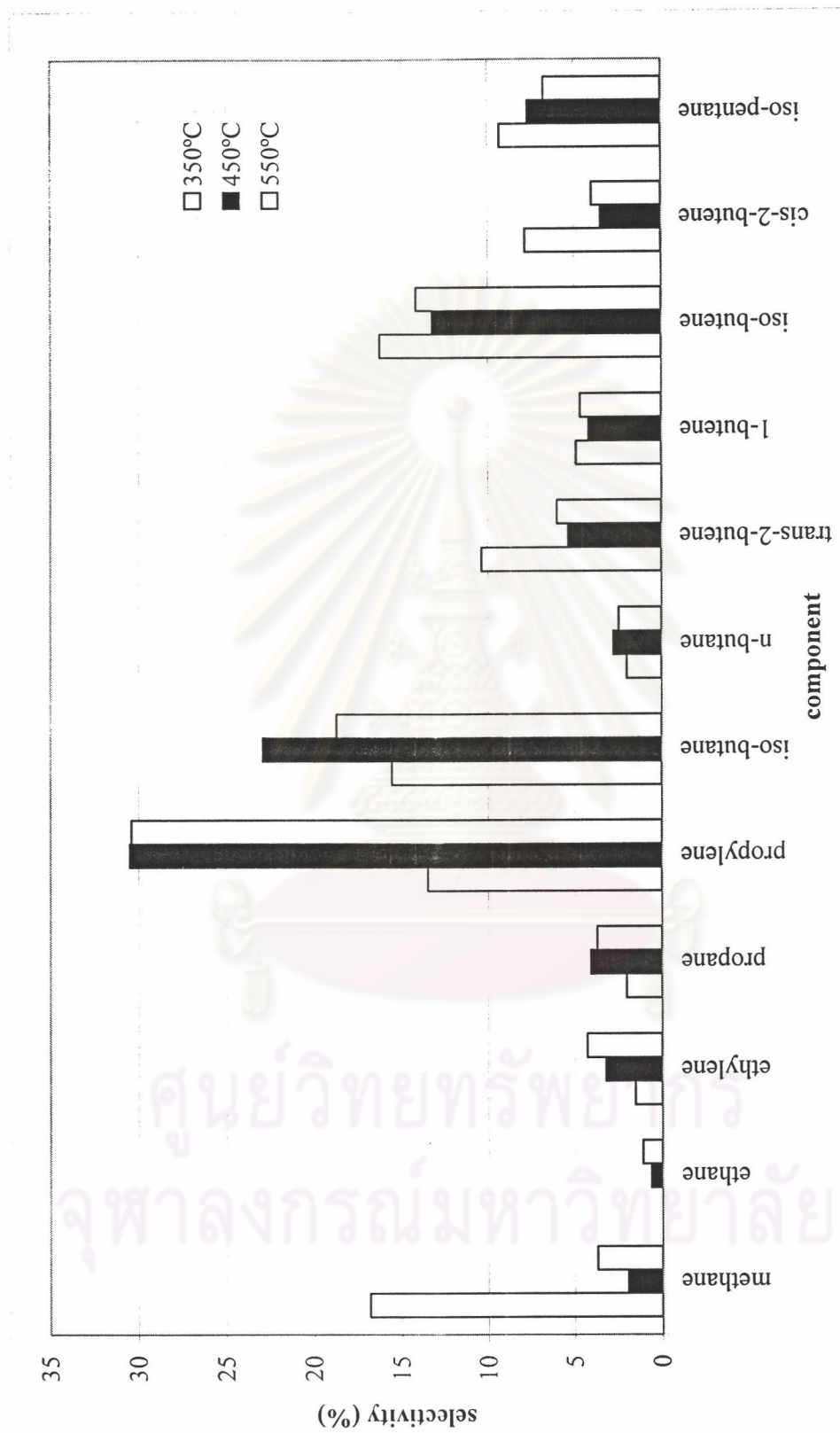


Figure 4.12 Product distributions in gas phase fraction obtained from the catalytic degradation of polyethylene over the H-MOR(127) catalyst with various temperatures.

Similarly to polypropylene cracking at various temperatures, polyethylene cracking gives the C9+ as a major fraction that was shown in Figure 4.13. The composition of each fraction is not much different except aromatics decrease from 30 to 20 and 15% with increasing temperature from 350 to 450 and 550°C, respectively. Indeed, aromatics are important fraction in liquid fuel because they are correspondent to octane number in gasoline. However, if propylene is the most required product, H-MOR with the Si/Al ratio of 127 is the most appropriate catalyst for degradation of polypropylene and polyethylene to give the highest selectivity to propylene formation with the least of coke and methane formation at the temperature of 450°C.

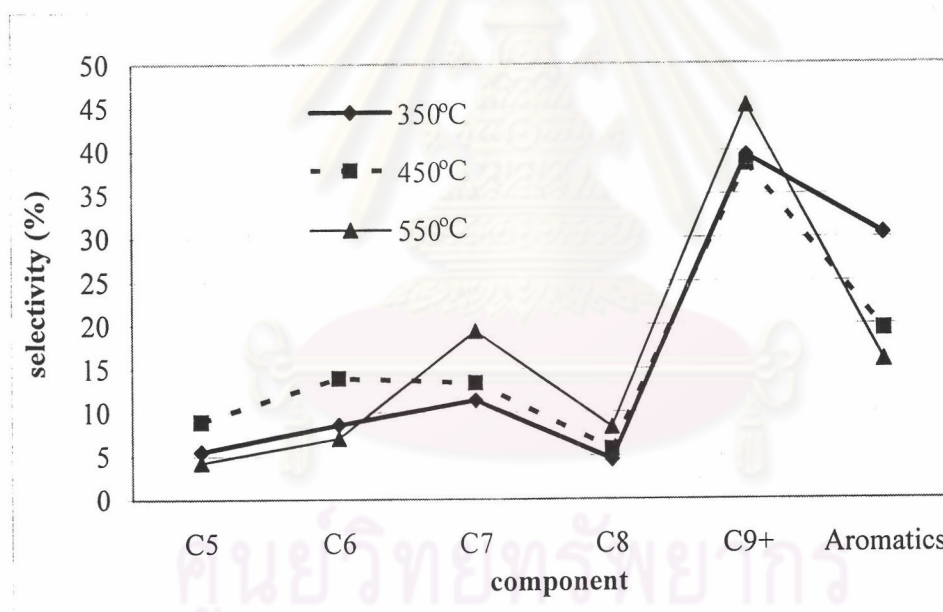


Figure 4.13 Product distributions in volatile liquid obtained from the catalytic degradation of polyethylene over the H-MOR(127) catalyst with various temperatures.