

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of the Dealuminated Mordenite

4.1.1 Degree of Sodium Exchange by Ammonium Ions

The analysis results of the sodium ions remained in the dealuminated mordenite, H-MOR samples are compiled in Table 4.1. The small content of sodium ions remained means that the large amount of the sodium ions in Na-MOR was replaced by exchanging ammonium ions, called degree of ammonium exchange. This results in the large amount of hydrogen ions or protons produced after the removal of NH_3 from the NH_4 -MOR samples by calcination at high temperature. Table 4.1 shows that among the dealuminated mordenite samples H-MOR(B) contains less amount of remained Na ions than H-MOR(A) while H-MOR(C) contains the least amount of remained Na ions, i. e. the ion exchange by Method C in Section 3.4 leads to the highest level of exchange of Na ions in mordenite by NH_4 ions. This is accounted by the difficult accessibility to Na ions located in small pores. For the low content of Na ions remaining in a zeolite the migration of the Na ions from small pores to 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. Therefore, Method C is chosen as the optimal method for preparing the dealuminated samples for the rest of this study.

Table 4.1 · The analysis results of the sodium ions left in the dealuminated mordenite and the corresponding degree of ammonium exchange in MOR samples

Sample Code	Remained Na Amount (% by weight)	Degree of NH ₄ Exchange (%)
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 using the ammonium exchange Method A.

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

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

4.1.2 XRD Results

The X-ray patterns of Na-MOR, H-MOR(A) and H-MOR(C) which are shown in Figure 4.1 show the characteristic pattern of MOR structure without any other phase of materials. This indicates that the MOR structure is intact by any mean of ammonium ion exchange.

4.2 Factors Involved in Dealumination of Mordenite

4.2.1 Effect of Temperature on Si/Al Ratio of Mordenite

To decrease the aluminum content, on the other hand to increase the Si/Al ratio in the zeolite the high aluminum-content H-MOR was dealuminated by acid leaching. The Si/Al ratios in the mordenite treated with a HCl solution of 1 M for 3 h at various temperatures were shown in Table 4.2. The acid treatment of the H-MOR (Si/Al = 11) between 90-120°C gives a relation that the higher the temperature is, the more the aluminum can be removed and thus the zeolite contains more Si/Al ratio.

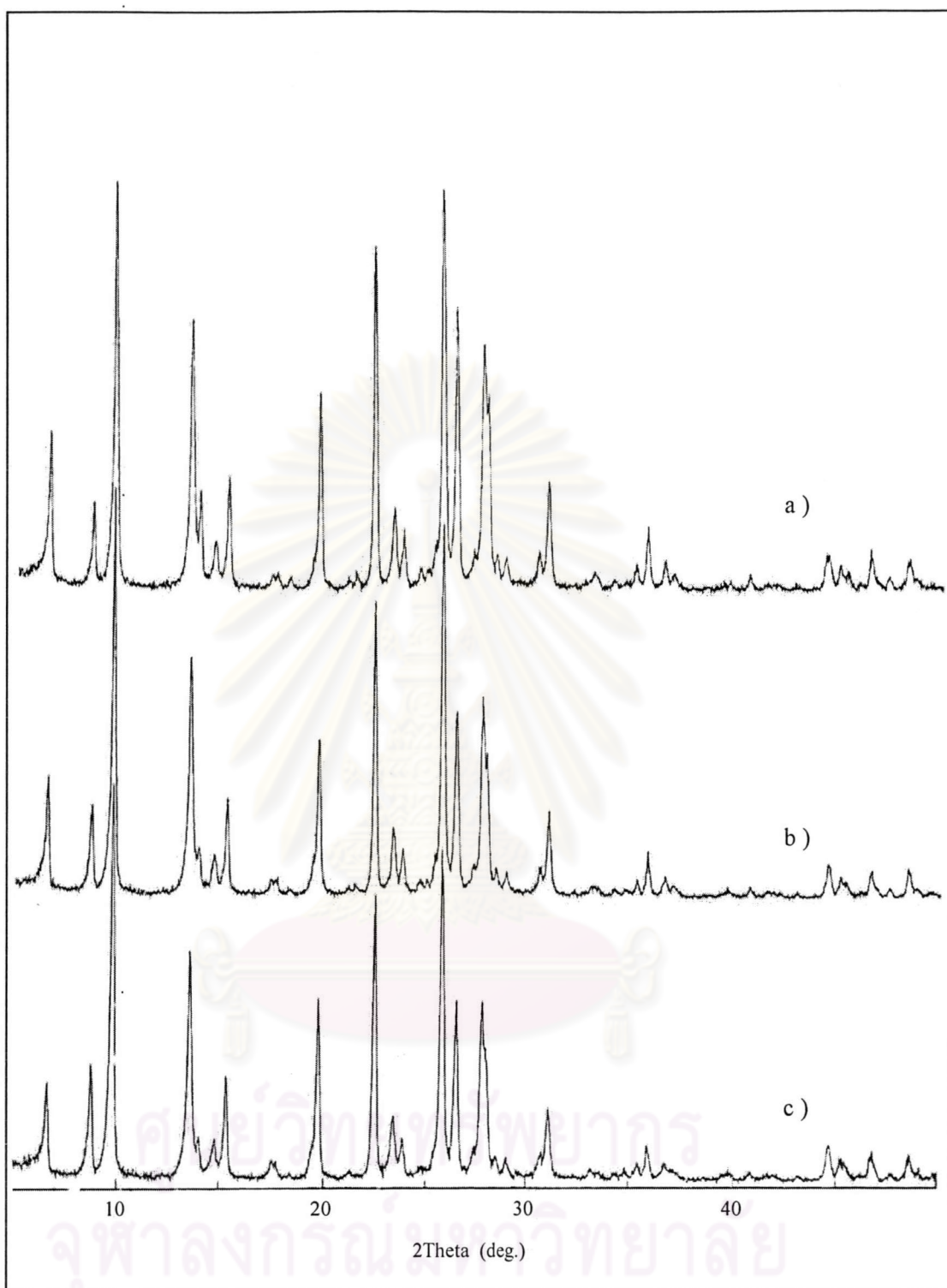


Figure 4.1 The X-ray patterns of H-MOR samples, a) Na-MOR, b) H-MOR(A) and c) H-MOR(C).

Table 4.2 The Si/Al ratios in the mordenite 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 the H-MOR treated with the HCl solution of 1 M for 3 h at different temperatures from 90-120°C. All NH₃-TPD profiles present two types of acid sites in the acid treated H-MOR samples. They are generally assigned⁴⁵⁻⁴⁶ 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,⁴⁵ 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 bridged oxygen atoms and thus the tetrahedral AlO₄⁵⁻ or empirically AlO₂⁻ needs a cation, here is H⁺ to balance the negative charge. This is known as the Brønsted acid site. The aluminum at the Brønsted acid site can transfer reversibly to a three-coordination type which 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.

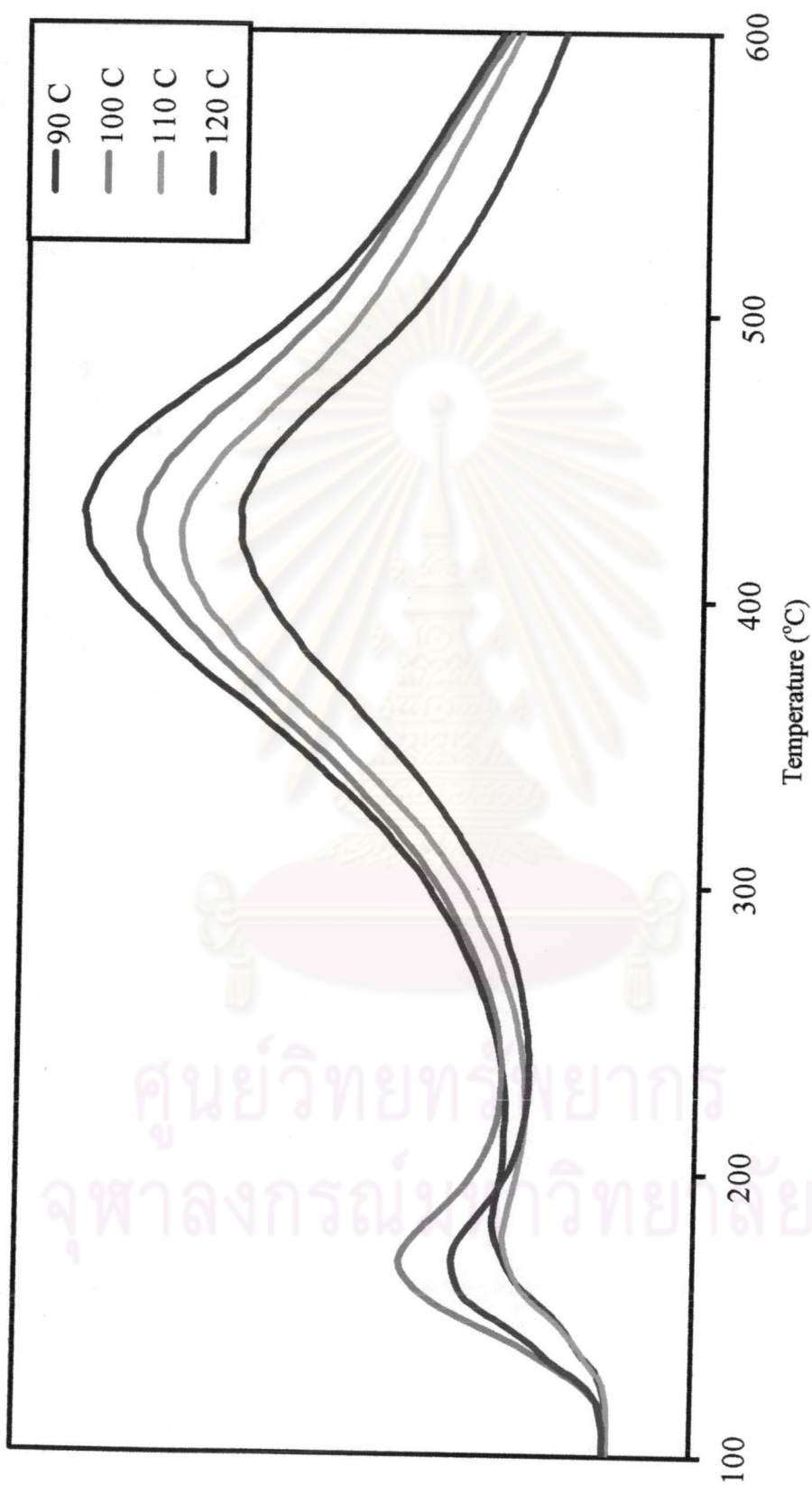


Figure 4.2 NH_3 -TPD profiles of dealuminated H-MOR prepared by acid leaching with hydrochloric acid of 1.0 M at various temperatures: 90°C (—), 100°C (—), 110°C (—) and 120°C (—)

4.2.2 Effect of HCl Concentration on Si/Al Ratio of Mordenite

The Si/Al ratios in the dealuminated H-MOR obtained from the acid leaching at 100°C using HCl of various concentrations ranging from 0.1 to 6.0 M are shown in Table 4.3 and Figure 4.3. Increasing the concentration of the HCl solution causes in obvious 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 from 2.0-6.0 M. The linear relation is represented by

$$Y = 13.25X + 10.5$$

when Y is the resulted 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 Figure 4.3. This indicates that if an extrapolation of the linear line is used, a mistake will be made.

The XRD of the H-MOR treated with the HCl solutions of 4.0 and 6.0 M were measured to ensure that the mordenite structure is not affected by the mineral acid treatment. The XRD results shown in Figure 4.4 have proven that the MOR structure is intact 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 40 and 80 may be prepared by using the HCl solution of 2.3 M and 5.5 M, respectively. The analysis result shows that the actual Si/Al ratios of the H-MOR catalysts are 39 and 73, respectively. The results are quite close to the expected ratios especially the one with Si/Al = 39. The XRD (not shown) of H-MOR (Si/Al = 39 and 73) are still unchanged.

Table 4.3 The Si/Al ratios in the mordenite 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

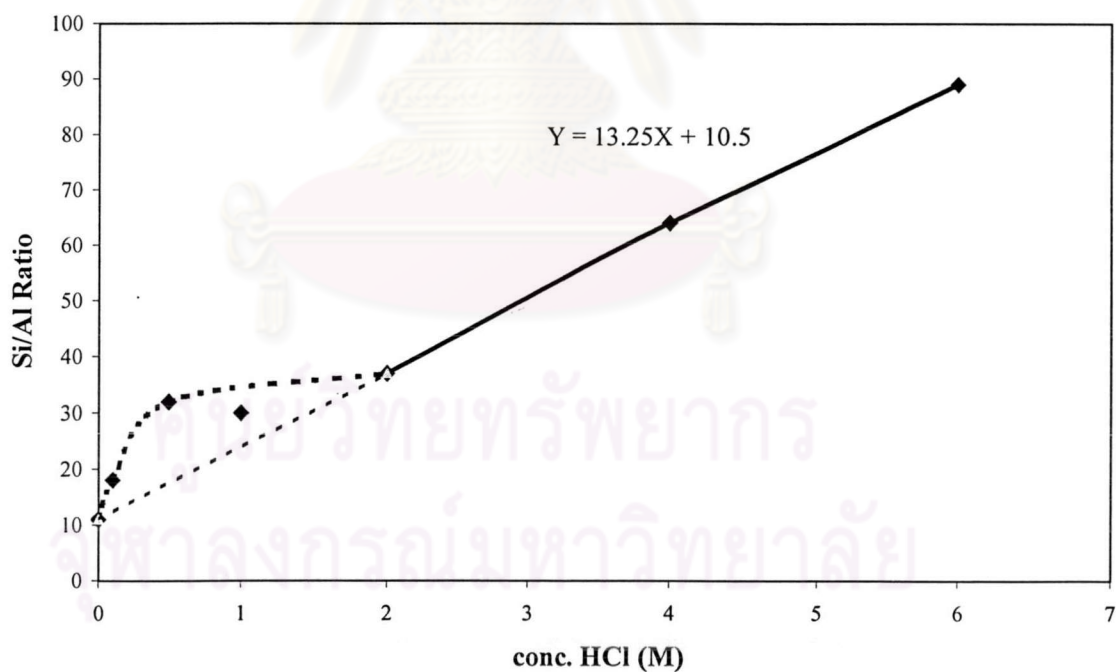


Figure 4.3 The relation between Si/Al ratios in the dealuminated mordenite and the HCl concentrations for the acid leaching of H-MOR at 100°C for 3 h.

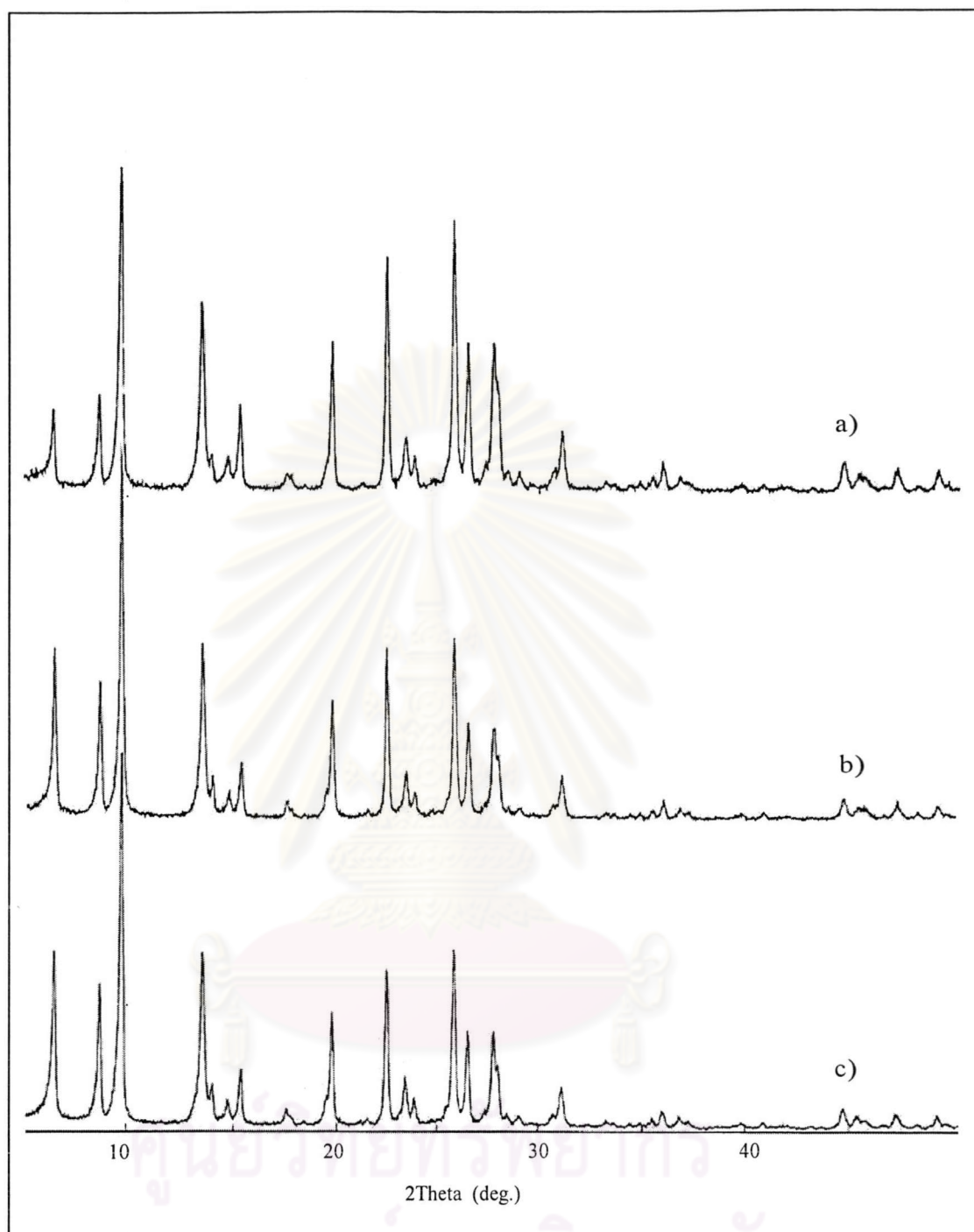


Figure 4.4 The X-ray diffractograms of H-MOR samples, a) as untreated H-MOR with Si/Al = 11, b) the H-MOR treated with 4.0 M HCl at 100°C for 3 h, and c) H-MOR treated with 6.0 M HCl at 100°C for 3 h.

4.3 ^{27}Al -NMR of the Dealuminated H-MOR (Si/Al = 39)

The ^{27}Al -NMR spectrum of the dealuminated H-MOR (Si/Al = 39) was shown in Figure 4.5. The most predominant peak at a chemical shift of 56 ppm belongs to the tetrahedral aluminum atoms in the framework structure of H-MOR. There is only a weak signal of the octahedral aluminum atoms located on the surface of the H-MOR. The ratio of peak height of the framework Al to non-framework Al is 8.2:1. This indicates that 90% of the aluminum atoms are located at the framework position while 10% of the aluminum atoms are at the non-framework position.

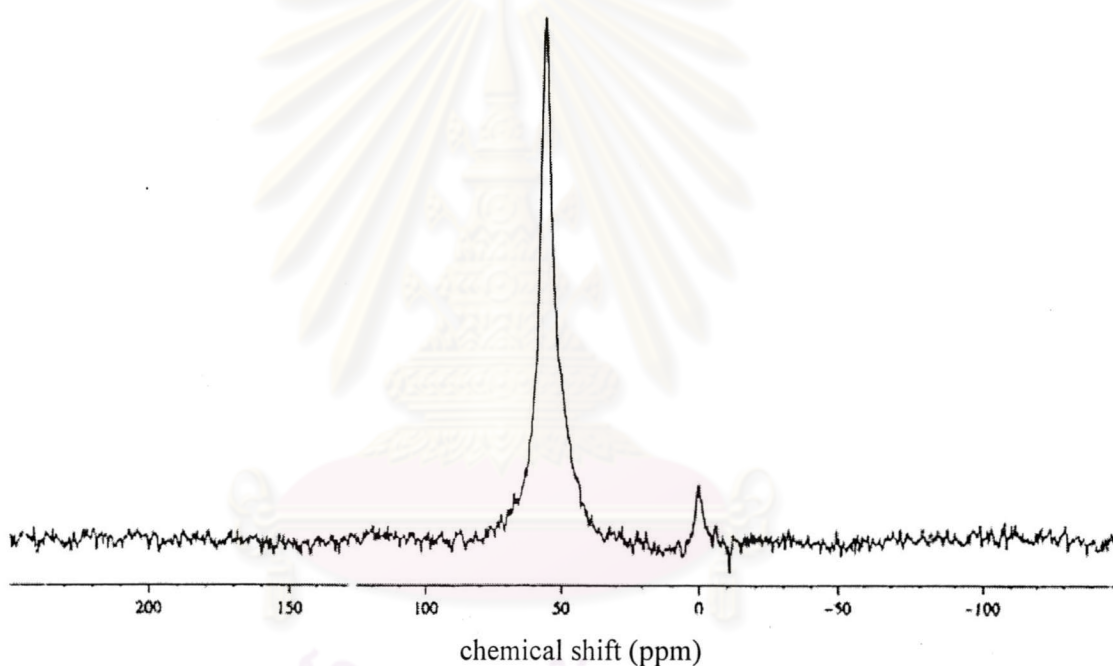


Figure 4.5. The ^{27}Al -NMR spectrum of the dealuminated H-MOR (Si/Al = 39) prepared by the acid leaching using a HCl solution of 2.3 M at 100°C for 3 h.

4.4 Catalytic Activity Tests of the Mordenite Catalysts

4.4.1 Effect of Time on Stream on Methanol Conversion

Methanol conversion and gas product distribution using H-MOR (Si/Al = 11) as the catalyst at various time on stream (TOS) of 20, 40 and 60 min are shown in Table 4.4. Time on stream has no effect on the conversion of the methanol which is 100% for all cases.

It affects the selectivity to C_2+C_3 olefins, which becomes the highest at TOS of 40 min, along with the least amount of alkanes (C_1-C_5). An amount of methane increases markedly with a longer exposure of the catalyst to the methanol feed. The reasons may be owing to the cracking of propane can occur at 500°C and the catalyst deactivation by hydrocarbon pool, namely coke. The formation of CO or CO_2 is in doubt due to the oxidation of hydrocarbon was suppressed by nitrogen atmosphere and the immiscible phase of water was formed obviously in a significant amount. Thus TOS of 40 min is chosen for the rest of the catalytic test.

Table 4.4 Methanol conversion and gas product distribution using H-MOR (Si/Al =11) as the catalyst at various time on stream (Conditions: 0.2 g of catalyst, feed at a GHSV of 2000 h^{-1} , $T_{MeOH} = 29^\circ C$, $T_{catalyst} = 500^\circ C$)

	Time on stream (min)		
	20	40	60
% Conversion	100	100	100
<u>Product Distribution (% mol)</u>			
- methane	66.5	73.9	79.1
- ethane	3.7	0.6	-
- ethylene	14.4	15.6	6.6
- propane	9.8	2.6	0.7
- propylene	2.9	5.6	4.4
- <i>iso</i> -butane	1.7	0.7	0.9
- <i>n</i> -butane	0.5	0.2	-
- <i>trans</i> -2- butylene	0.1	0.2	1.7
- <i>I</i> -butylene	0.1	0.2	1.0
- <i>iso</i> -butylene	0.2	0.3	4.0
- <i>cis</i> -2-butylene	0.1	0.1	1.3
- <i>iso</i> -pentane	0.2	0.2	0.4
C_2+C_3 olefins (% mol)	17.3	21.2	11.0
Alkanes (C_1-C_5) (% mol)	82.4	78.2	81.1

4.4.2 Effect of Temperature on Methanol Conversion

Methanol conversion and gas product distribution using H-MOR (Si/Al =11) as the catalyst at various catalyst temperatures (300, 350, 400, 450 and 500°C) are shown in Table 4.5. The conversion of methanol is complete at the temperatures from 350°C to 500°C. The methanol conversion becomes markedly decreased at the temperatures below 350°C. At elevated temperatures especially at 500°C, methane is formed in a significant amount due to the competitive cracking of hydrocarbons over the acid H-MOR catalyst to smaller molecules. This phenomenon results in the decrease of the amount of larger C₃ and C₄ alkanes and the increase of methane and ethane. The highest selectivity to ethylene and propylene is obtained at the temperature of 450°C. The selectivity decreases with the change of the lower temperatures. At 500°C, the conversion of olefins to liquid hydrocarbons causes the decrease in the amounts of high olefins.

In all cases, the liquid product content is the major products. In the liquid products, water is speculated as principal product and heavy paraffins as minor content because water is obtained from the condensation of methanol during the conversion to hydrocarbon products.

4.4.3 Effect of Si/Al Ratio of the Catalysts on Methanol Conversion

4.4.3.1 Effect of Si/Al Ratio at High Temperature

Methanol conversion and product distribution using H-MOR with various Si/Al ratios (11, 38, 73 and 120) at 500°C are shown in Table 4.6 and Figure 4.6. At 500°C, there is no difference in the conversions of methanol which is completed in all cases. The H-MOR (Si/Al = 11) provides the highest methane content and coke formation which obviously decreases when Si/Al ratio in the catalysts increases. Ethylene and propylene (C₂+C₃ olefin) increase with increasing the Si/Al ratio in H-MOR but the total content of alkanes decreases. The yields of alkanes, liquid products and coke are distinctly decreased with increasing Si/Al ratio of H-MOR.

Table 4.5 Methanol conversion and gas product distribution using H-MOR (Si/Al =11) as the catalyst at various temperatures of the catalyst (Conditions: 0.4 g of catalyst, feed at GHSV of 2000 h⁻¹, T_{MeOH} = 29°C, time on stream = 40 min)

	Temperatures (°C)				
	300	350	400	450	500
% Conversion	89.7	100	100	100	100
<u>Product Distribution (% mol)</u>					
- methane	44.2	20.6	24.2	41.2	64.7
- ethane	0.2	1.3	2.4	3.5	3.4
- ethylene	33.1	11.2	12.6	14.2	12.9
- propane	11.8	48.5	45.8	29.2	11.7
- propylene	1.9	1.1	3.2	4.0	3.4
- <i>iso</i> -butane	5.6	10.2	6.2	4.8	2.5
- <i>n</i> -butane	1.7	6.0	4.4	2.3	0.7
- <i>trans</i> -2- butylene	0.3	0.1	0.2	0.2	0.1
- <i>l</i> -butylene	0.1	0.0	0.1	0.1	0.1
- <i>iso</i> -butylene	0.6	0.1	0.3	0.0	0.3
- <i>cis</i> -2-butylene	0.2	0.0	0.1	0.5	0.1
- <i>iso</i> -pentane	0.3	0.8	0.5	0.1	0.2
C ₂ +C ₃ olefins (% mol)	35.0	12.3	15.8	18.2	16.3
C ₂ -C ₄ olefins (% mol)	36.2	12.5	16.5	18.9	16.9
C ₁ -C ₅ alkanes (% mol)	63.8	87.4	83.5	81.1	83.2
Yield of gas product (%wt.)	25.4	35.9	11.8	14.3	10.2
Yield of liquid product (%wt.)	57.4	47.4	71.6	66.4	70.3
Coke (% wt. of catalyst)	9.6	9.7	10.1	10.7	11.5

Table 4.6 Methanol conversion and gas product distribution using various the Si/Al ratios of H-MOR as the catalyst at 500°C of catalyst (Conditions: 0.4 g of catalyst, feed at GHSV of 2000 h⁻¹, T_{MeOH} = 29°C, time on stream = 40 min)

	Si/Al ratio of H-MOR			
	11	39	73	120
% Conversion	100	100	100	100
<u>Product Distribution (% mol)</u>				
- methane	64.7	19.9	6.5	6.0
- ethane	3.4	1.5	0.8	0.6
- ethylene	12.9	24.1	28.1	26.9
- propane	11.7	28.8	19.4	14.1
- propylene	3.4	9.0	23.1	32.4
- <i>iso</i> -butane	2.5	11.7	15.9	14.0
- <i>n</i> -butane	0.7	3.1	2.3	1.5
- <i>trans</i> -2- butylene	0.1	0.3	0.7	0.8
- <i>I</i> -butylene	0.1	0.2	0.5	0.7
- <i>iso</i> -butylene	0.3	0.7	1.5	1.9
- <i>cis</i> -2-butylene	0.1	0.2	0.5	0.5
- <i>iso</i> -pentane	0.2	0.5	0.6	0.5
C ₂ +C ₃ olefins (% mol)	16.3	33.1	51.2	59.3
C ₂ -C ₄ olefins (% mol)	16.9	34.5	54.4	63.2
C ₁ -C ₅ alkanes (% mol)	83.2	65.5	45.5	36.8
Yield of gas product (%wt.)	10.2	32.6	43.0	52.8
Yield of liquid product (% wt)	70.3	55.6	47.5	40.2
Coke (% wt of catalyst)	11.5	6.5	5.2	3.7

From Figure 4.6 on H-MOR with the Si/Al ratio of 120, the selectivity to olefins is the highest while the yields of alkanes, liquid product and coke are the least. The removal of the framework aluminum and the reaction of the number of strong acid sites permits the mordenite to be a very good catalyst for conversion of methanol into light olefins

with a very high selectivity as well as with overcoming the problem of coke formation on the used catalyst.

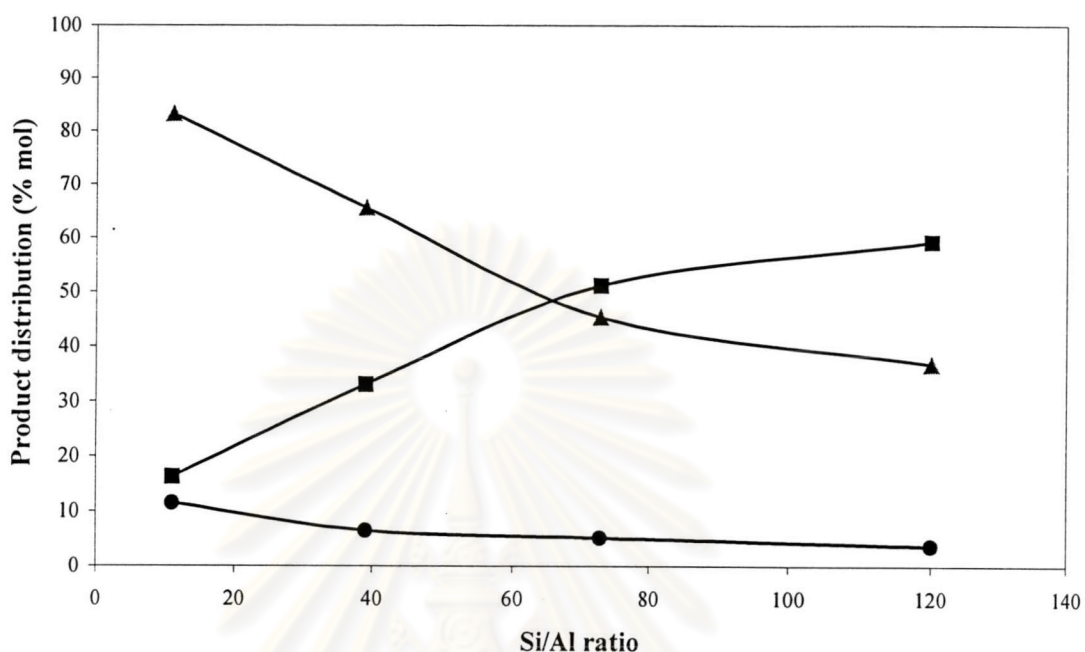


Figure 4.6 Gas-product distribution in methanol conversion using various Si/Al ratios of H-MOR at 500°C, GHSV 2000 h⁻¹ and time on stream = 40 min.

■ = % selectivity to C₂+C₃ olefins, ▲ = %selectivity to alkanes (C₁-C₅),
● = %wt Coke

Considering Figure 4.7, the selectivity to propylene increases while the selectivity to propane decreases with decreasing the aluminum content in H-MOR. The explainable reason of the result involves Brønsted acid sites in the catalyst. At the low Si/Al ratio the catalyst has many Brønsted acid sites. Protonation or the hydrogen transfer from the Brønsted acid sites occurs in the final step of the reaction as the conversion of light olefins to paraffin. The gradual reduction of number of acid sites decreases the probability of the interaction of light olefin molecules with protons. Therefore, the conversion of light olefins into alkanes is decreased while the Si/Al ratio of catalyst is increased.

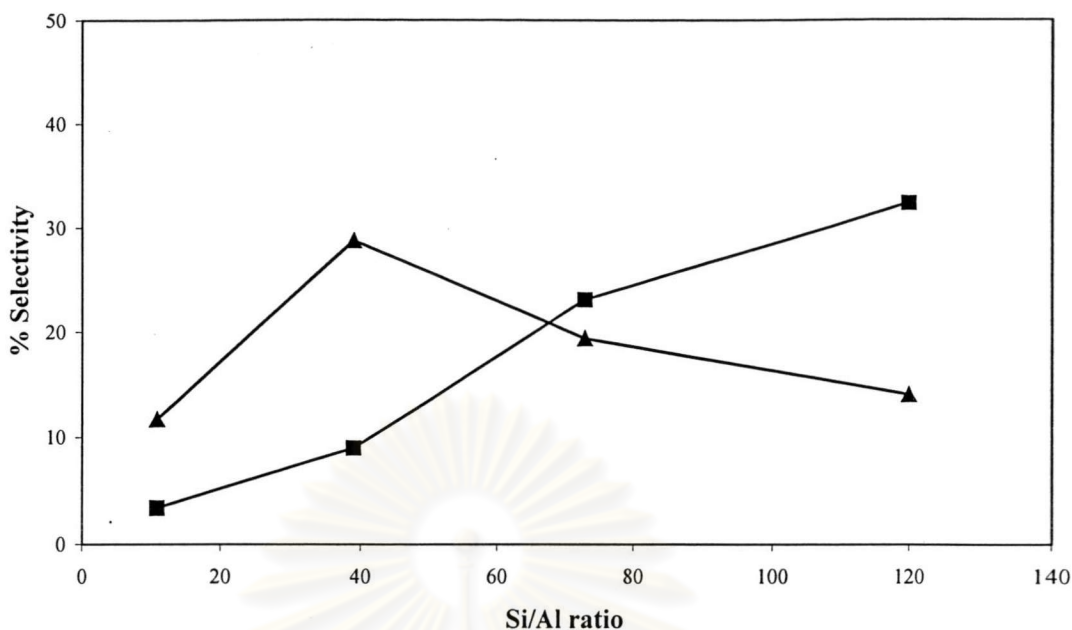


Figure 4.7 Selectivity to propylene and propane affected by the Si/Al ratios of the H-MOR catalyst in methanol conversion at 500°C of catalyst (Conditions: 0.4 g of catalyst, feed at GHSV of 2000 h⁻¹, T_{MeOH} = 29°C, time on stream = 40 min).

■ = propylene, ▲ = propane

4.4.3.2 Effect of Si/Al Ratio at Low Temperature

Methanol conversion and product distribution using H-MOR with various Si/Al ratios at 300°C are shown in Table 4.7. It was found that catalytic activity is nearly complete in all cases, except at the Si/Al ratio of 120. The activity of H-MOR (Si/Al = 120) is the least. With increasing the Si/Al ratio or reducing the aluminum content, the selectivity to C₂+C₃ olefin tends to increase but the selectivity to alkanes tends to decrease. The result is similar to that at 500°C. For all cases at the temperature of 300°C, the selectivity to alkanes is higher than that to olefins. *iso*-Butane is a major gas product. The amount of liquid product and coke deposited are slightly reduced when the Si/Al ratio is increased from 11 to 120.

Table 4.7 Methanol conversion and gas product distribution using H-MOR with various the Si/Al ratios as the catalyst at 300°C of catalyst (Conditions: 0.4 g of catalyst, feed at GHSV of 2000 h⁻¹, T_{MeOH} = 29°C, time on stream = 40 min)

	Si/Al ratio of H-MOR			
	11	39	73	120
% Conversion	89.7	88.8	88.7	78.8
<u>Product Distribution (% mol)</u>				
- methane	44.2	16.5	10.8	9.1
- ethane	0.2	0.1	0.1	-
- ethylene	33.1	28.1	22.0	23.1
- propane	11.8	8.5	4.8	3.0
- propylene	1.9	3.0	11.4	16.1
- <i>iso</i> -butane	5.6	40.6	43.6	44.6
- <i>n</i> -butane	1.7	1.1	1.0	0.4
- <i>trans</i> -2- butylene	0.3	0.1	0.5	0.7
- <i>l</i> -butylene	0.1	0.1	0.2	0.3
- <i>iso</i> -butylene	0.6	0.1	1.0	1.3
- <i>cis</i> -2-butylene	0.2	1.8	4.6	0.4
- <i>iso</i> -pentane	0.3	-	-	1.2
C ₂ +C ₃ olefins (% mol)	35.0	31.1	33.4	39.2
C ₂ -C ₄ olefins (% mol)	36.2	33.2	39.7	41.9
C ₁ -C ₅ alkanes (% mol)	63.8	66.8	60.3	58.3
Yield of gas product (%wt.)	25.4	21.9	25.7	31.8
Yield of liquid product (% wt)	57.4	64.2	62.4	60.0
Coke (% wt of catalyst)	9.6	7.7	6.8	4.7

4.4.4 Lifetime of the Catalysts

Methanol conversion was carried out at a GHSV 2000 h⁻¹, temperature of 500°C, feed of 20% methanol vapor balanced with nitrogen and atmospheric pressure. The conversions of methanol are compared using H-MOR catalysts with Si/Al ratio of 11 and

120. The initial conversion of methanol is complete and not different in both cases as shown in Figure 4.8. At time on stream of 100 min, the catalyst with Si/Al ratio of 11 is slightly deactivated. Methanol conversion on the other catalyst is complete and remained constant on 480 min (8 h). Catalyst lifetime of dealuminated H-MOR can be estimated from the conversion in the same duration of time on stream. Catalyst lifetime increases gradually with the decrease of number of Brønsted acid sites. Similarly, in a study conducted by Campbell *et al.*,⁴⁶ MTO over H-ZSM-5 catalyst showed that the dramatically longer catalyst lifetimes of H-ZSM-5 with higher Si/Al ratio were much longer than H-ZSM-5 with lower Si/Al ratio after repeated utilization.

The rapid deactivation of H-MOR (Si/Al = 11) may be explained by coke formation on the external surface and inside of the partially blocked pores of the catalyst, which can block the entrance of the one-dimensional channels. That leads to a drastic decrease of the concentration of the Brønsted acid centers available for reacting with the substrate molecules.

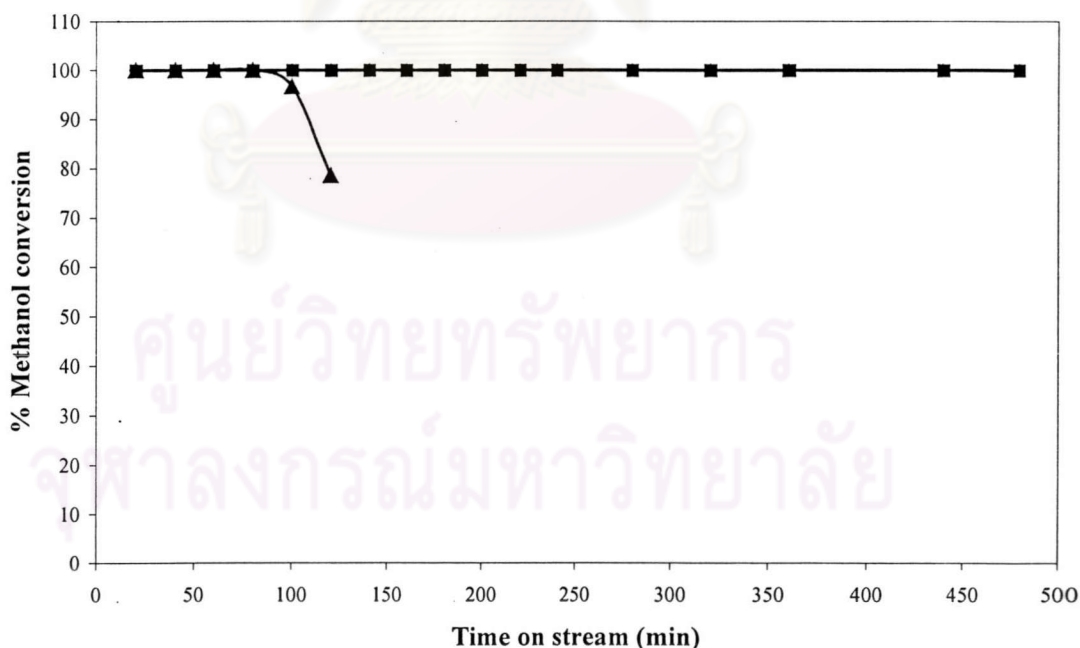
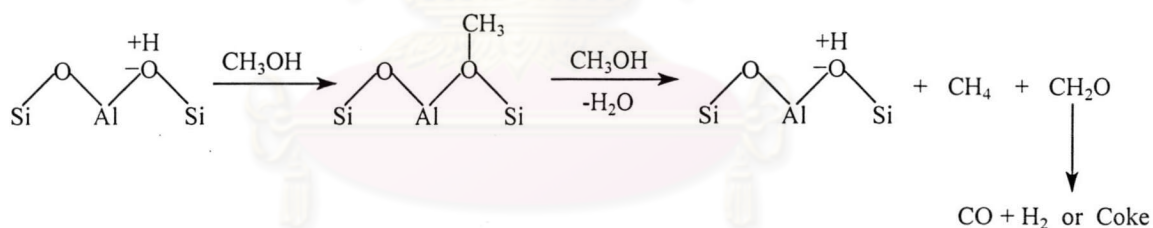


Figure 4.8 Methanol conversion on H-MOR with Si/Al ratio = 11 and 120, at 500°C and GHSV 2000h⁻¹: ▲ = Si/Al of 11, ■ = Si/Al of 120.

4.4.5 Catalytic Deactivation

4.4.5.1 Effect of Temperature on Coke Formation on Catalyst

Table 4.8 shows the relation of coke formation and the methane content with various reaction temperatures. Coke formation and the methane content slightly increase with increasing the reaction temperature. The catalyst rapidly deactivates. Enhancement in methane selectivity during the deactivation of zeolite catalysts in the methanol conversion reaction has been commented previously and is considered to be due to enhanced hydride donation to a surface methoxy intermediate. The loss of activity is considered to be associated with coke formation on the active sites. Deactivation and methane formation were highly essential features, with respect to the reaction mechanism in Scheme 4.1. There was no doubt that the formation of methoxy groups was an important first step of the methanol interaction with the acid sites. Further interaction of these methoxy groups with other methanol molecules adsorbed around the acid sites might cause not only a C-C bond formation but also transformations leading to desorption of methane in the gaseous phase and a residue formation on the surface.



Scheme 4.1 Methane and coke formation pathway.

Table 4.8 Coke formation on the H-MOR (Si/Al = 11) catalyst at various temperatures (Conditions: 0.4 g of catalyst, feed at a GHSV of 2000 h⁻¹, T_{MeOH} = 29°C, time on stream = 40 min)

	Temperatures (°C)			
	350	400	450	500
Methane (% mol.)	20.6	24.2	41.2	64.7
Coke (% wt.)	9.7	10.1	10.7	11.5

4.4.5.2 Effect of Si/Al Ratio on Coke Formation on Catalysts

Amounts of coke deposited on the H-MOR catalyst with various Si/Al ratios at 300 and 500°C are shown in Figure 4.9. In both cases, coke formation distinctly decreases with increasing the Si/Al ratio of catalyst which the coke content on the catalyst with Si/Al of 120 is the least. The result is in agreement with the decrease of methane content (Tables 4.6 and 4.7) and the increase of catalyst lifetime (Figure 4.8). The rate of coke formation for a number of methanol conversion is found to decrease with the reduction in aluminum content. The results are similar to those previously observed by others.^{1,14,15} The effect of the Si/Al ratio of dealuminated mordenite on coke formation is in line with using dealuminated H-beta¹³ and dealuminated H-ZSM-5⁴⁷ catalysts. The amounts of coke deposited on the H-MOR catalyst at 500°C is less than that at 300°C.

The density of acid sites would have a strong influence on coke forming reactions, particularly intermolecular hydrogen transfer, so that overall catalyst performance was improved when the number of acid sites is decreased. Coke formation in methanol conversion had been shown to occur in two stages: initial formation of internal coke poisoning acid sites within the zeolite pores, followed by coke deposition on the external surface. It was only during this latter stage of coke formation, the methanol conversion was completely suppressed.⁵³

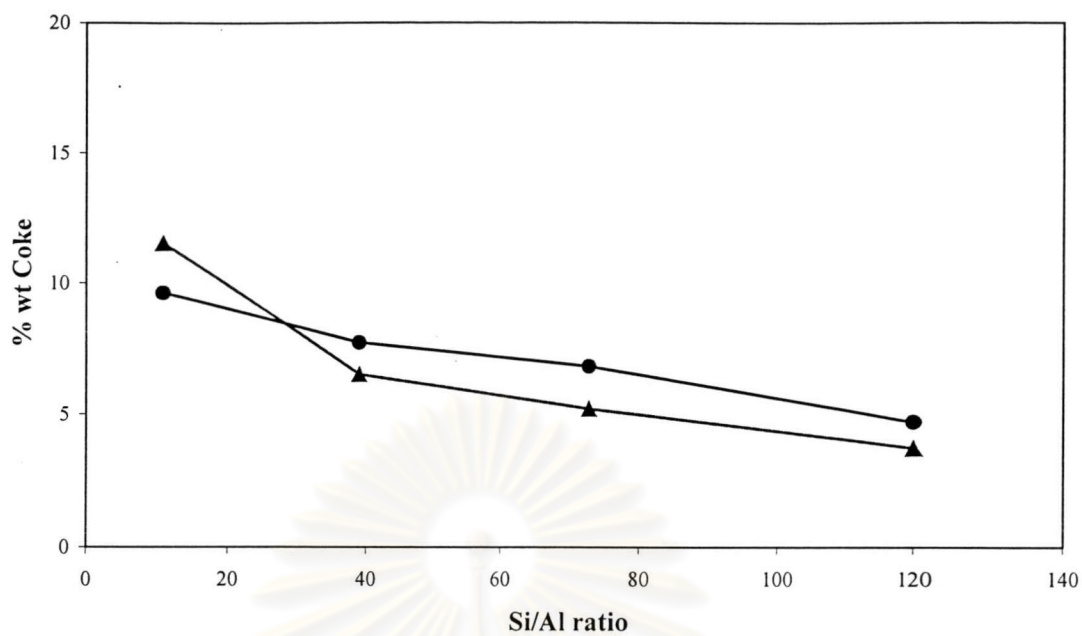


Figure 4.9 Coke formation on H-MOR with various Si/Al ratios in methanol conversion at 300°C (●) and 500°C (▲).

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย