

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Materials Obtained from Various Synthesis Methods

In this report, three methods of synthesis of Al-MCM-41 have been attempted: (A) Synthesis under acidic condition; (B) One-temperature synthesis under basic condition; (C) Two-temperature synthesis under basic condition. Actually the first method (A) was performed according to Aguado's method<sup>62-63</sup> for synthesis of Al-MCM-41 while the methods (B) and (C) were modified from Huang's method<sup>64</sup> for synthesis of a composite ZSM-5/MCM-41 using dual templates TPABr and CTAB. In our methods (B) and (C), the starting mixture contained no TPABr, which was the pore-directing agent for ZSM-5. In Huang's synthesis method, it was believed that the first step was formation of nucleation centers at the pH of 12 for mesoporous structure of MCM-41 at the temperature of 100°C for 2 days and the second temperature of 125°C was essential for formation of microporous ZSM-5. The pH was reduced to 9.5 for prevention of transformation of ZSM-5 to quartz that was readily at the high pH. However, formation of MCM-41 continued at 125°C after the nucleation centers had been formed. The temperature of 125°C was considered not necessary for formation of mesoporous MCM-41. Therefore, both one-temperature synthesis at 100°C and two-temperature synthesis at 100°C and then 125°C were then attempted in parallel in this study.

XRD patterns of the as-synthesized products obtained from each synthesis method are shown in Figure 4.1. The XRD pattern in Figure 4.1(A) shows no reflection peaks at small Bragg's angles between 1.5 and 10°. The result indicates that

Al-MCM-41 can not be formed readily under acidic condition. This may be accounted for the scarce report in synthesis of Al-MCM-41 under acidic condition. XRD patterns in Figure 4.1(B) and (C) show the characteristic peaks of MCM-41 structure similar to that of MCM-41 reported by Beck.<sup>33-34</sup> The observation of four peaks which can be assigned to a hexagonal lattice. The sharp peak observed at  $2\theta$  of  $2.0^\circ$  ascribes to the reflection on (100) lattice plane and the rest of weak intensities at  $2\theta$  of  $3.68^\circ$ ,  $4.22^\circ$  and  $5.54^\circ$  correspond to the reflection of (110), (200), and (210) planes, respectively. This is obvious that there is a shift of (100) reflection peak to lower value of  $2\theta$ ,  $2.00^\circ$  compared to the peak position at  $2.20^\circ$  of pure silica MCM-41. The peak shift implies that in some extent silicon is substituted by aluminum in the framework. Furthermore, XRD pattern of the Al-MCM-41 sample obtained from the two-temperature synthesis is much greater in peak intensities than those of the sample obtained from the one-temperature synthesis. It is believed that the pH controlled at 9.5 can accelerate the formation of the mesoporous structure of MCM-41 in the presence of aluminum. According to the sharp feature of the XRD pattern of the product obtained from method (C), the synthesis condition also allows the formation of structure with long-range order. The pH of gel for Al-MCM-41 formation is lower than that for pure silica MCM-41 formation that is generally about 11-12. The silicon content was determined by XRF and the aluminum content was by both XRF and ICP-AES. The analysis results by XRF and ICP-AES techniques both agree to each other that the Al-MCM-41 contains Si/Al ratio of 17 which is similar to the ratio in gel. Therefore further study on synthesis of Al-MCM-41 was carried out using the two-step synthesis method under basic condition.

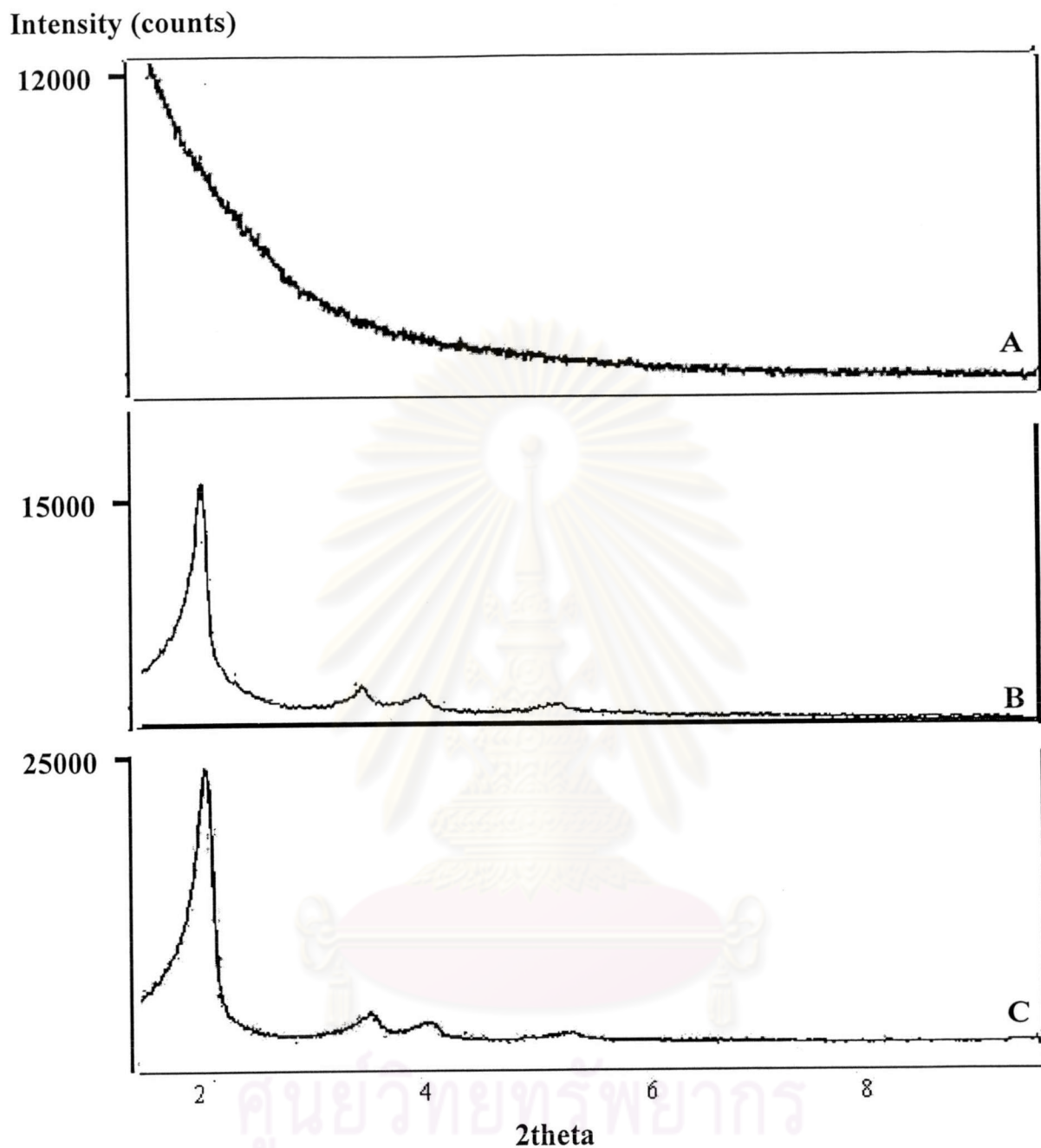


Figure 4.1 XRD patterns of the as-synthesized products obtained from three different methods: (A) Synthesis under acidic condition; (B) one-temperature synthesis under basic condition; (C) two-temperature synthesis under basic condition.

## 4.2 Al-MCM-41 with Various Si/Al Ratios

### 4.2.1 XRD Results

Using the two-temperature synthesis method (C) with pH adjustment Al-MCM-41 with Si/Al ratios in gel of 17, 20, 40, 60 and 80 were prepared. XRD patterns of all products are shown in Figure 4.2. It was found that all XRD patterns are similar and they present four characteristic peaks of the MCM-41 structure. The intensity of the (100) reflection peak increases with the increase of Si/Al ratio in gel. The result indicates that the lower aluminum content, the higher order of the structure because the low aluminum content can highly disperse in the structure.

### 4.2.2 XRF and ICP-AES Data

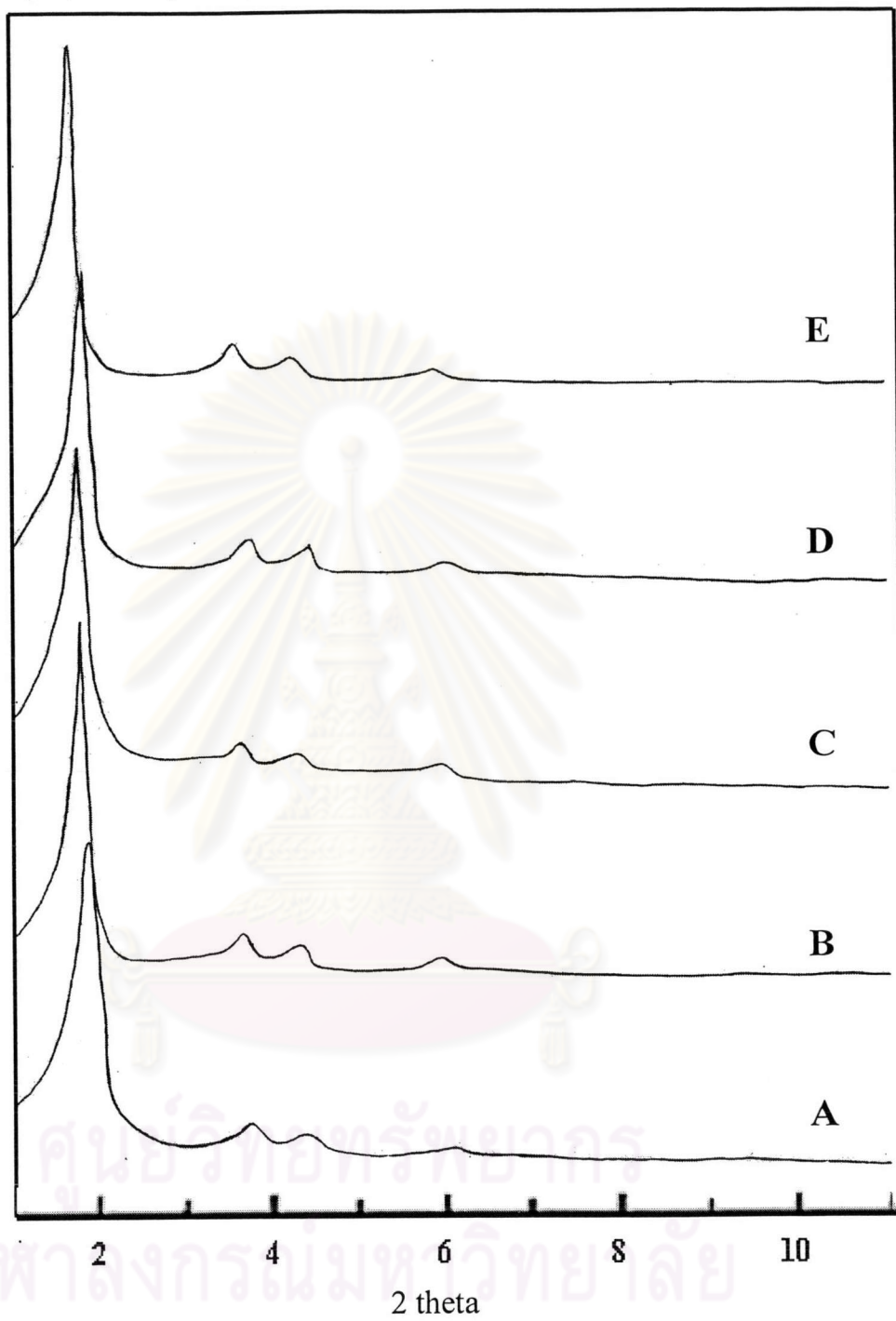
The Si/Al ratios in gel and in product of the Al-MCM-41 are compared in Table 4.1. It is acceptable that the Si/Al ratios in product are roughly close to the Si/Al ratios in gel. The result suggests that the products obtained really contain aluminum.

**Table 4.1** Si/Al ratios in gel and in product of Al-MCM-41 samples

Sample	Si/Al ratio in gel	Si/Al ratio in product analyzed by XRF	Si/Al ratio in product analyzed by ICP-AES
Al-MCM-41-20	20	22.79	23.50
Al-MCM-41-40	40	44.60	48.37
Al-MCM-41-60	60	60.41	64.48
Al-MCM-41-80	80	88.17	79.02



Intensity (arbitrary unit)

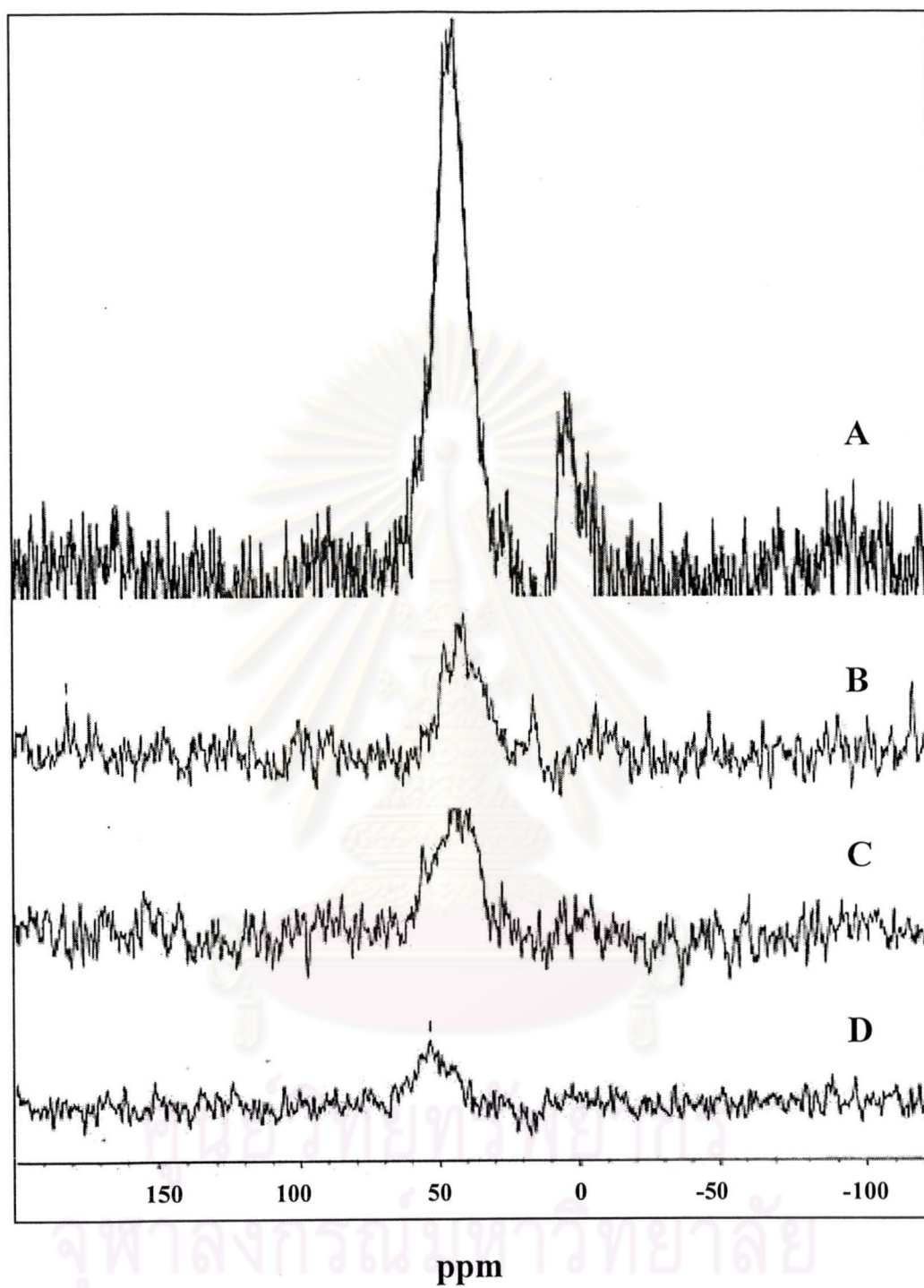


**Figure 4.2** XRD patterns of the as-synthesized products with different Si/Al ratio in gel: (A) 17; (B) 20; (C) 40; (D) 60; (E) 80.

### 4.2.3 Solid-State $^{27}\text{Al}$ -NMR Spectra

To determine whether the aluminum atoms are at the framework site or non-framework site, solid-state  $^{27}\text{Al}$ -NMR spectra can provide such information. Solid-state  $^{27}\text{Al}$ -NMR spectra of calcined Al-MCM-41 samples with different Si/Al ratio are presented in Figure 4.3. The NMR spectra exhibit the presence of two aluminum signals at the chemical shifts of 56 and 0 ppm. Typically, the former signal refers to the framework site and the latter signal ascribes to the non-framework site.<sup>65</sup> At low aluminum content (Si/Al = 60-80), it seems to present only the framework position. With increasing the aluminum content (Si/Al = 20-40), the signals increase at both sites. All samples exhibit similarly that the signal of the framework site is more pronounced than that of the non-framework site. That means aluminum atoms mainly locate at the framework site rather than the non-framework site. It should be noted that the as-synthesized Al-MCM-41 sample shows only the signal at the framework site of aluminum atoms. Removal of the template leads to the appearance of the signal at 0 ppm due to the dealumination of the framework aluminum to the octahedral coordinated aluminum at the extra-framework site. This is in accordance with reported in literature.<sup>66</sup> This is the first report of successful synthesis of Al-MCM-41 using the two-temperature synthesis method.

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**Figure 4.3** Solid-state  $^{27}\text{Al}$ -NMR spectra of as-synthesized Al-MCM-41 with different Si/Al ratio in gel: (A) 20; (B) 40; (C) 60; (D) 80.

#### 4.2.4 NH<sub>3</sub>-TPD Profiles

NH<sub>3</sub>-TPD profiles of calcined Al-MCM-41 samples with different Si/Al ratios of 20, 40 and 60 are plotted in Figure 4.4. The results show only one asymmetric broad ammonia desorption peak with a maximum at 200°C. This peak is due to the presence of Brønsted acid sites<sup>66</sup> that interacts with basic ammonia molecules. The type of adsorbed ammonia is capable of releasing upon heating the sample to the range of 200 to 265°C<sup>51, 67-68</sup> depending on the preparation methods. Lack of a ammonia desorption peak at the temperature of 400°C indicates the absence of stronger Lewis acid sites. This is in agreement with other reports for Al-MCM-41. Increasing the aluminum content, or decreasing the of Si/Al ratio, causes the increase in peak area corresponding to the amount of desorbed ammonia. That is the number of acid sites or acidity of the Al-MCM-41 catalyst increases with the aluminum content in the catalyst. However, the active site for polymer degradation is known as Brønsted acid sites or protons. Thus the Al-MCM-41 samples are expected to exhibit their catalytic activity in polymer degradation. NH<sub>3</sub>-TPD of calcined Al-MCM-41 samples with Si/Al ratio of 80 was not measured.



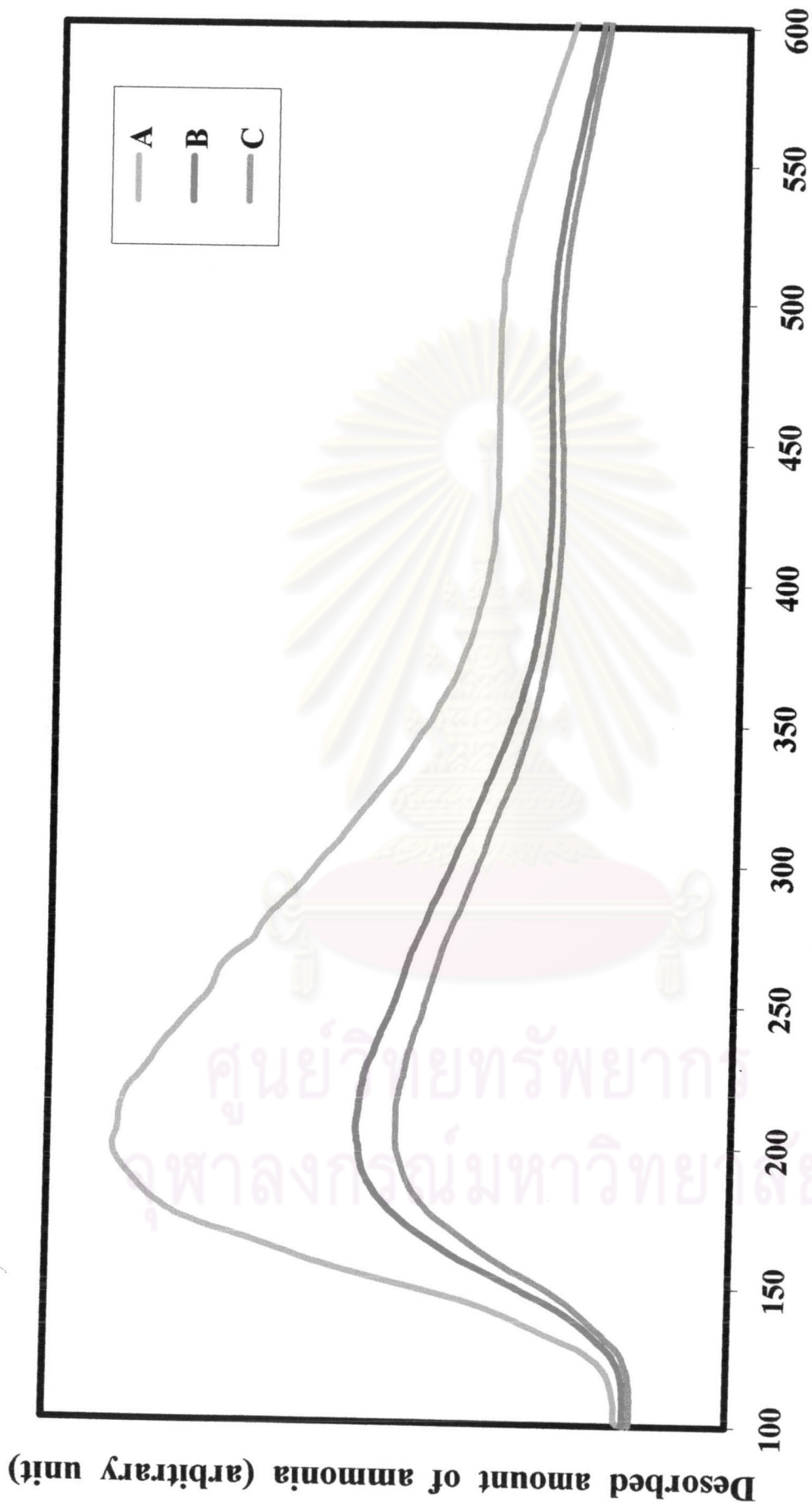


Figure 4.4 NH<sub>3</sub>-TPD profiles of calcined Al-MCM-41 samples with different Si/Al ratio in gel: (A) 20; (B) 40; (C) 60.

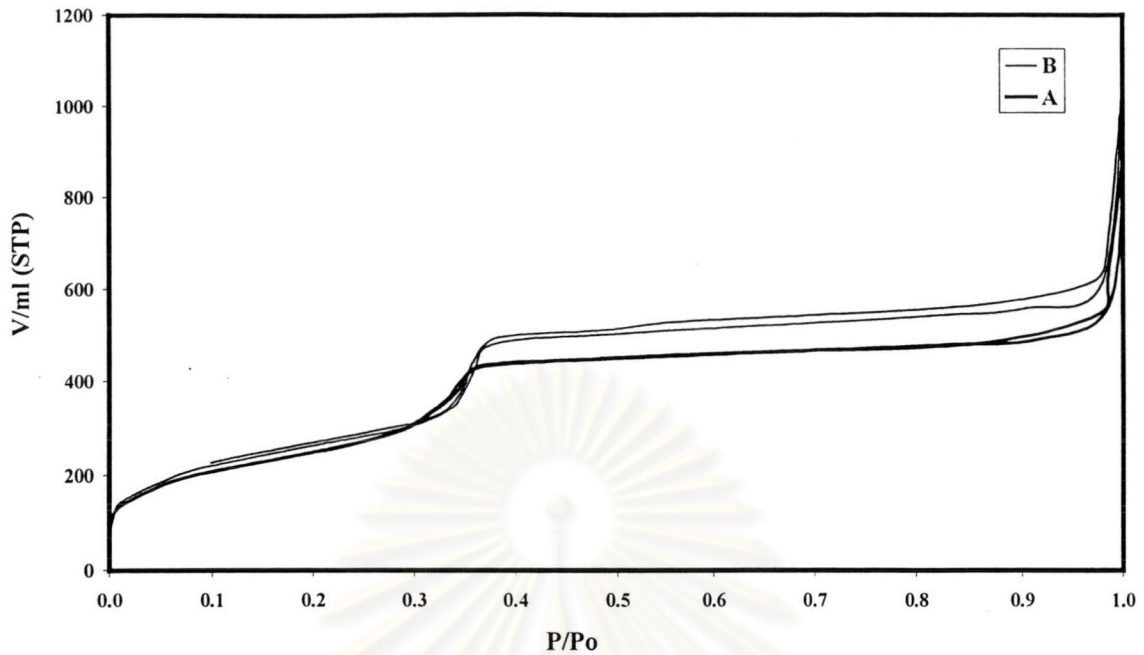
#### 4.2.5 Nitrogen Adsorption

Adsorption isotherms of nitrogen on Al-MCM-41 samples with different Si/Al ratio at  $-196^{\circ}\text{C}$  are shown in Figure 4.5. Each isotherm shows type IV character, which is a typical feature for mesoporous MCM-41. The adsorbed amount increases gradually with increasing relative pressure by multilayer adsorption. A steep rise in the adsorbed amount is observed at a relative pressure of 0.3-0.4, being caused by capillary condensation of nitrogen in the mesopores. This rise become more gentle and is shifted to lower relative pressure with increasing aluminum content, which suggests that the pore size distribution is narrowed.<sup>66</sup> This is in accordance with reported in literature.<sup>38, 51, 69-71</sup> The Brunauer, Emmett, and Teller (BET) specific surface area of samples analyzed by the nitrogen adsorption is ranged between 906.34 and 954.33  $\text{m}^2/\text{g}$  as shown in Table 4.2. The Al-MCM-41 samples still have very high surface area over other types of catalysts.

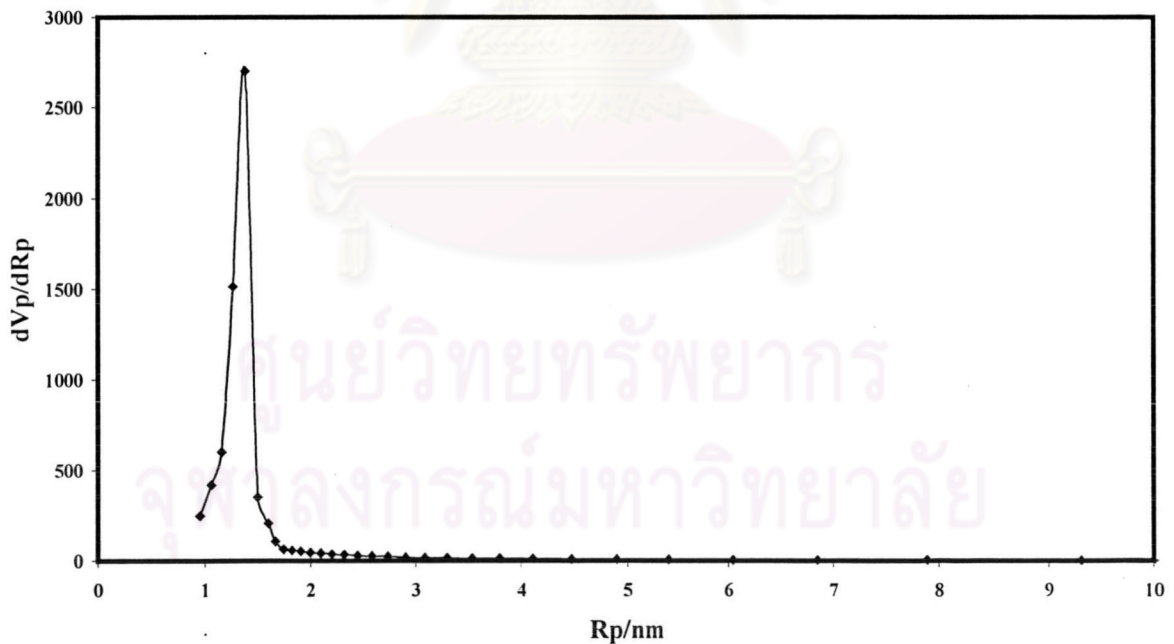
**Table 4.2** Some physicochemical properties of Al-MCM-41

Samples	Si/Al (gel)	BET surface area ( $\text{m}^2/\text{g}$ )	Average pore diameter (nm)
Al-MCM-41	20	906.34	2.86
Al-MCM-41	80	954.33	2.86

In estimation of pore size distribution of mesoporous materials by nitrogen adsorption measurements, the Dollimore-Heal (DH) method, which considers the thickness of multilayer adsorption, provides a better estimation than the Barret, Joyner, and Halenda (BJH) method.<sup>66</sup> Pore size distribution curves of Al-MCM-41 samples estimated by the DH plot applied on the adsorption branch of each isotherm are shown in Figure 4.6. The pore size distribution curve of both samples had a sharp peak centered at the pore radius of 1.43 nm or diameter of 2.86 nm.



**Figure 4.5** Adsorption-desorption isotherm of nitrogen on Al-MCM-41 with Si/Al ratio of 20 (A) and 80 (B) at  $-196^{\circ}\text{C}$ .



**Figure 4.6** Pore size distribution of Al-MCM-41 (Si/Al = 20) obtained by nitrogen adsorption at  $-196^{\circ}\text{C}$ .

#### 4.2.6 Template-free Al-MCM-41

XRD patterns of the samples measured after the removal of organic template from the pores of Al-MCM-41 by calcination at 540°C were shown in Figure 4.7. The XRD data reveal that the organic template affects the intensities of the reflection peaks especially the parent one, in XRD patterns. In the absence of the template, the peak intensity is twice that in the presence of the template in pores. The less intensity in the latter case results from screening of some diffracted radiation by the template and the rest is let to the detector of the XRD. This effect is in common observed for zeolites and other porous materials.

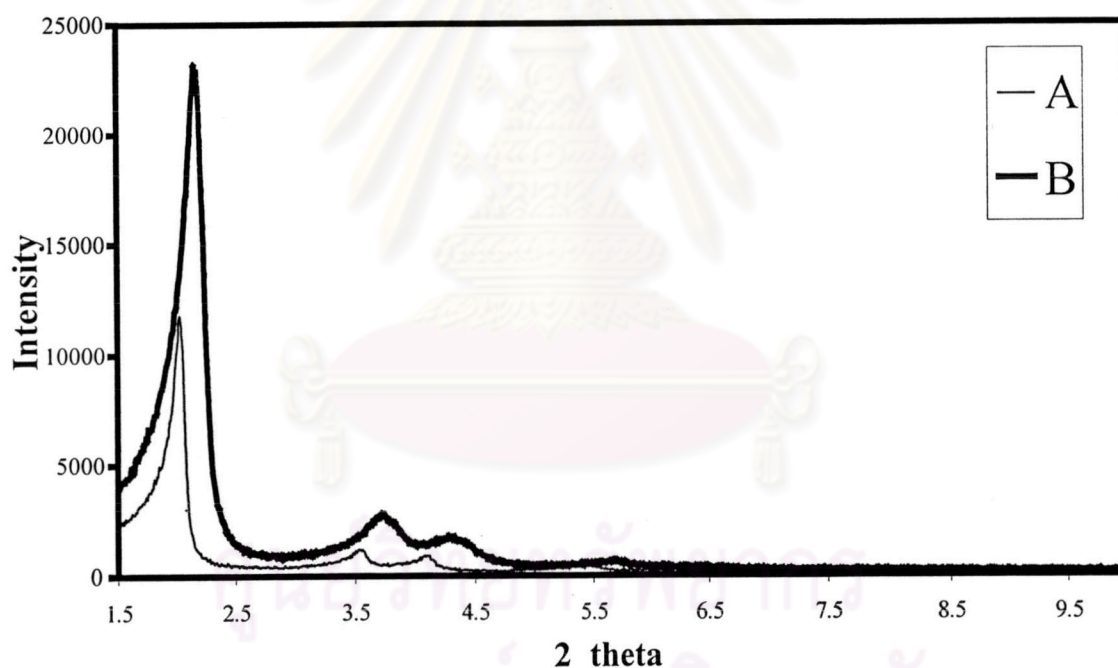


Figure 4.7 XRD patterns of the as-synthesized (A) and calcined (B) Al-MCM-41.



### 4.3 Catalytic Activity of Al-MCM-41 in Degradation of Polypropylene

#### 4.3.1 Effect of Temperature on the Activity of Al-MCM-41

##### 4.3.1.1 The Values of %conversion and Product Yield

The values of %conversion and product yield obtained from the catalytic degradation of polypropylene using Al-MCM-41 with the Si/Al of 20 at various temperatures of 350, 450 and 550°C are compared in Table 4.3. It is found that the activity of Al-MCM-41 catalyst in degradation of polypropylene is very high even at as low temperature as 350°C. In the present study, conversions of polypropylene are almost 100% at temperature ranged from 350 to 550°C. At the lowest temperature of 350°C, degradation products are mainly in liquid phase which decreases in amount at higher temperatures. In contrast, the yield of products in gaseous phase is the least at this temperature and increases with increasing temperature. Formation of coke is found in all cases and falls in the range of 6.4 to 8.8%. Coke tends to increase at higher temperatures.

**Table 4.3** Values of %conversion and product yield obtained in the catalytic degradation of polypropylene using Al-MCM-41 with Si/Al of 20 at various temperatures

	Temperature (°C)		
	350	450	550
conversion of propylene (%)	97	98	100
Yield of gas (% wt of propylene)	23	57	71
Yield of liquid (% wt of propylene)	68	31	21
coke (% wt of catalyst)	6.4	8.8	8.4

Usually, zeolite catalysts are stronger acidic than MCM-41, and even Al-MCM-41, therefore cracking of hydrocarbons such as LDPE is more readily over stronger acidic zeolites than MCM-41 and weaker acidic Al-MCM-41.<sup>37</sup> On the contrary, the cracking of HDPE and PP took place over zeolite HZSM-5 at much lower %conversion<sup>37</sup> of polymer than that over the weaker acidic Al-MCM-41. Those results are in agreement with that from this study. This is obviously not resulted from the effect of strong acidity but rather from the limitation of diffusion in the zeolite channels. The bulky high molecular weight polypropylene causes the inaccessibility to the active Brønsted acid sites on the catalyst with too small channels but no steric effect in mesoporous Al-MCM-41. With the Si/Al ratio in gel of 20 and very high surface area the Al-MCM-41 proves that it contains enough Brønsted acid sites to conduct the propylene cracking.

The yield of liquid fraction is greater than that at high temperature while the gas fraction is formed at higher temperatures. This can be accounted by the following reasons. By increasing temperature polypropylene decomposes to degraded polymer which presents less molecular weight. The thermal cracking may get involved at this step. In addition, the external surface area of Al-MCM-41 is available for primary degradation to degrade polymer and subsequently smaller intermediates such as liquid fraction. When the degraded polymer and the liquid fraction diffuse into the hexagonal channels, this is the mean of removal product from the primary cracking resulting in acceleration of the primary cracking of the polymer. Although liquid fraction has greater mobility than that of degraded polymer and oligomers, it may not be able to undergo secondary cracking at low temperature. With increasing temperature, secondary cracking can then take place in the channels of Al-MCM-41 to yield smaller products such as aromatics and can go further to as small products as gaseous olefins.

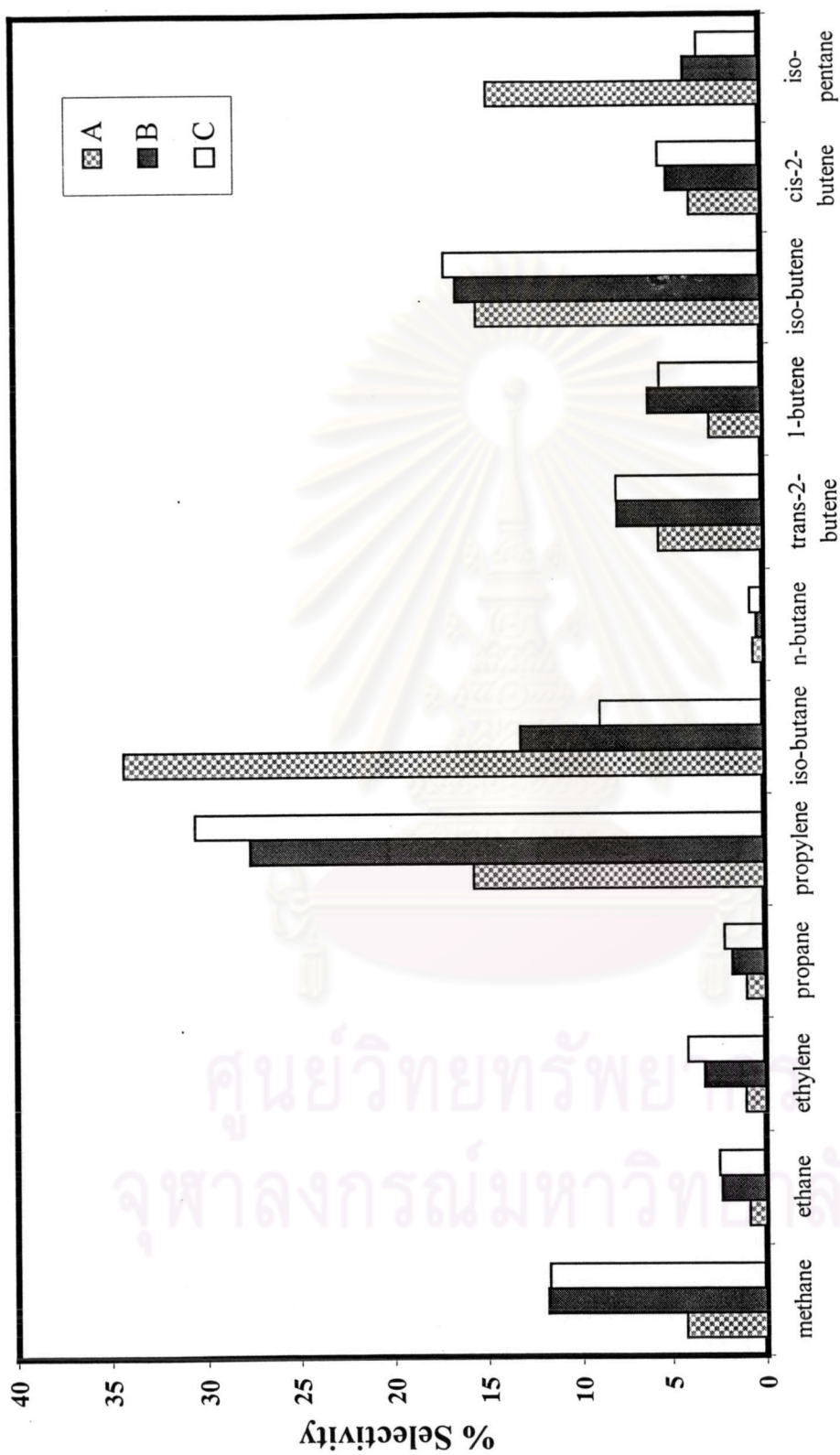
#### 4.3.1.2 Product Distribution of the Gaseous Phase

Distribution of gaseous products obtained from catalytic degradation of polypropylene over Al-MCM-41 with the Si/Al ratio in gel of 20 at various temperatures was shown in Figure 4.8. Formation of each gas is not significantly different at temperature of 450 and 550°C. Among gaseous products formation of *iso*-butane is favored at 350°C while formation of propylene is favored at high temperatures. Isomerization of 1-butene to its isomers is observed at 350°C and isobutene is found as the major product among isomeric butenes. At higher temperatures of 450 and 550°C, *iso*-butane can be readily converted to propylene and methane while *iso*-pentane can be readily converted to butenes and methane. Ethane, ethylene, propane and coke are formed in small amount due to cracking of hydrocarbons at elevated temperature. It is noted that the ethylene amount is greater when the reaction temperature increases. The catalyst became gray in color after utilization at each temperature. All turned to white again after regeneration at elevated temperature. By considering the highest selectivity to light olefins especially propylene and the lowest selectivity to *iso*-butane and *iso*-pentane, the reaction temperature of 550°C is preferred for further studies of variations in degradation of polypropylene.

#### 4.3.1.3 Product Distribution of the Volatile Liquid Fraction

Product distribution of the volatile liquid fraction obtained from catalytic degradation of polypropylene over Al-MCM-41 with the Si/Al ratio of 20 at various temperatures is shown in Figure 4.9. Each hydrocarbon was identified by a number of carbon atoms in a molecule including its isomers, for example, C<sub>9-14</sub> represents for a combination of aliphatic molecules containing nine carbon atoms to fourteen carbon atoms. The data show that the liquid fraction covers a broad range of hydrocarbons. The C<sub>9-14</sub> fraction is formed with the most selectivity in volatile liquid products at each temperature. With increasing temperature, selectivity to C<sub>9-14</sub> increases incredibly with increasing temperature and at the same time, lighter hydrocarbons of C<sub>5</sub> to C<sub>9</sub> tends to be





**Figure 4.8** Distribution of gaseous products obtained from the catalytic degradation of polypropylene over the Al-MCM-41 with Si/Al ratio of 20 at various reaction temperatures: (A) 350°C; (B) 450°C; (C) 550°C.



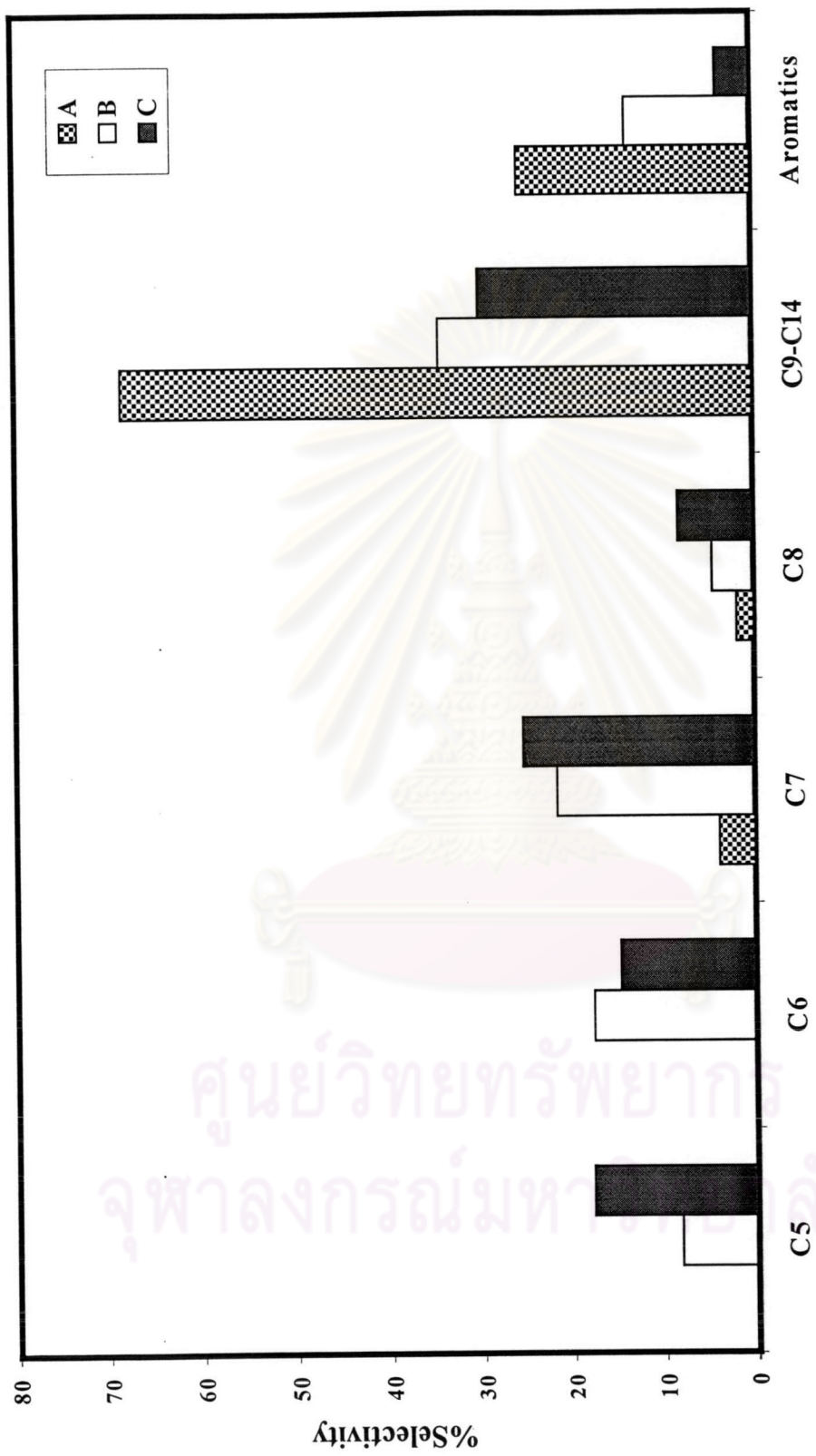


Figure 4.9 Product distribution of volatile liquid fraction obtained from catalytic degradation of polypropylene over Al-MCM-41 with the Si/Al ratio of 20 at various reaction temperatures: (A) 550°C; (B) 450°C; (C) 350°C.

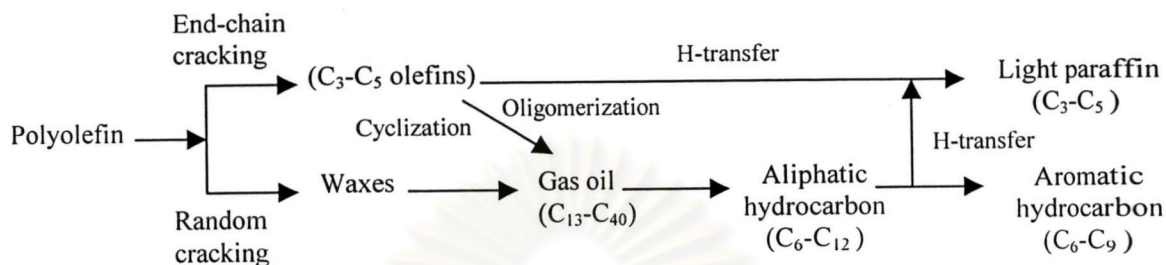
decrease. This phenomenon appears obvious at 550°C and is in agreement with that observed by Aguado<sup>36</sup> that heavier liquid products were formed in a greater amount with increasing temperature. It was postulated that at high temperature, oligomerization, a reverse reaction of cracking, took place at such a condition. Formation of aromatics is also in a similar trend.

The obtained selectivities can be related to the acid strength and pore structure of the catalyst. The heavier hydrocarbon fractions can be formed according to two pathway: oligomerization reaction of the olefinic gaseous fractions and random cracking at any position of the polymer chain. An increase in temperature may promote the oligomerization of light olefins, which also causes significant change in the product distribution.

On the basis of the results discussed earlier in section 4.3.1.3, the reaction scheme shown in Figure 4.10 is proposed to explain the catalytic conversion of the polypropylene over the Al-MCM-41 catalyst. In the case of the Al-MCM-41 catalyst, the cracking reaction occurs mainly within the uniform mesoporous structure, where steric hindrances are not present, mainly through random cracking reactions, yielding waxes as the primary products, at least in the initial cracking steps. The mild acidity and large pore size of this catalyst promotes a random scission mechanism that is responsible for the formation of heavy products, such as the waxes that remain in the reactor. Further cracking of these waxes yields gasoil and gasoline fractions.

Accordingly, each type of catalyst leads to a different prevailing polypropylene cracking mechanism : end-chain scission over ZSM-5 because of its high acid strength and random scission over Al-MCM-41 as a consequence of its mesoporosity and weaker acidity. Nevertheless, a certain contribution of the alternative cracking pathway should not be completely neglected for each catalyst.

Thus, random scission reactions can occur over the ZSM-5 zeolite, mainly on the external acid sites, whereas end-chain cracking reactions are also present to some extent over the Al-MCM-41 material.<sup>5, 36-37</sup>



**Figure 4.10** Reaction pathways in the conversion of the polypropylene.

In addition, there was a further markedly increased in aromatic yield with increasing temperature of catalytic reaction. An increase in temperature may promote the development of secondary reactions from the primary cracking products, such as the oligomerization and aromatization of gaseous olefins.<sup>72</sup> The formation of aromatics from olefins, mainly light hydrocarbon fractions, involves several sequential steps : olefin oligomerization, cyclization and dehydrogenation by hydrogen transfer.

From this result, the degree of oligomerization depends on the temperatures, because of the increasing temperatures will make the products to have a much of kinetic energies after cracking takes place. Then, the small products, have much of kinetic energies, become oligomerization.

### 4.3.2 Effect of Si/Al Ratio on the Activity of Al-MCM-41

#### 4.3.2.1 The Values of %conversion and Product Yield

Using the Al-MCM-41 with various Si/Al ratios in degradation of polypropylene at the temperature of 550°C, results in a variation of product yields as shown in Table 4.4. The conversion of propylene is not significantly affected by the change in Si/Al ratio of the Al-MCM-41 catalyst. With increasing Si/Al ratio, the yield of gas products slightly decreases and the yield of liquid fraction increases. The obvious change is on coke formation that can be reduced from 8.4% to 5.0%. This is accounted by the decrease in aluminum content, when the Si/Al ratio was increased, results in the reduced amount of Brønsted acid sites. This is in agreement with other acid zeolite catalysts such as mordenite<sup>73</sup> and ZSM-5.<sup>31</sup>

**Table 4.4** Values of %conversion and product yield obtained in the catalytic degradation of polypropylene using the Al-MCM-41 catalysts with various Si/Al ratios at the temperature of 550°C

	Catalyst			
	Al-MCM-41(20)	Al-MCM-41(40)	Al-MCM-41(60)	Al-MCM-41(80)
Conversion of propylene (%)	100	100	99	97
Yield of gas (% wt)	71	69	68	65
Yield of liquid (% wt)	21	26	27	28
Coke (% wt of catalyst)	8.4	6.5	5.0	5.0



#### 4.3.2.2 Product Distribution of the Gaseous Phase

Product distribution of gas products obtained from using the Al-MCM-41 with various Si/Al ratios in degradation of polypropylene at the temperature of 550°C is shown in Figure 4.11. For all cases in this study, the amount of product is in the order of propylene > *iso*-butene > coke. The product distribution in gaseous phase is very slightly different upon changing the Si/Al ratio in the catalyst. However, a trend of increasing selectivity to propylene and *iso*-butene can be observed with a trend of decreasing the selectivity to *iso*-butane. This observation is similar to that affected by increasing temperature.

#### 4.3.2.3 Product Distribution of the Volatile Liquid Fraction

Product distribution in volatile liquid fraction obtained from catalytic degradation of polypropylene over Al-MCM-41 with various Si/Al ratios at the temperature of 550°C is shown in Figure 4.12. At the low Si/Al ratio in catalyst C<sub>9-14</sub> fraction is favored while at higher C<sub>5</sub> fraction is favored. With increasing the Si/Al ratio in the catalyst from 20 to 40, 60 and 80, the selectivity to C<sub>9-14</sub> drastically decreases from 68 to 47, 12 and 7.7%, respectively. In contrast, selectivity to smaller component such as C<sub>5</sub> is much increased, *i.e.* from 0 to 13, 52 and 67%, respectively. Owing to no change in the yield of liquid fraction, C<sub>9-14</sub> must be converted to lighter hydrocarbons, mainly C<sub>5</sub> and some C<sub>6</sub> which are condensed as liquid products.

#### 4.4 Regenerated Catalysts

The sample of used Al-MCM-41 catalyst with the Si/Al of 20 turns to white after regeneration by calcination at 540°C for 6 h. Coke deposited in the used catalyst can be removed by the oxidation with air to carbon dioxide. XRD patterns of the freshly calcined unused and the regenerated catalyst samples are depicted in Figure 4.13. There is not significant change in intensity of the reflection peaks that are characteristics of Al-MCM-41 structure. This data prove that the structure of Al-MCM-41 is stable at the cracking conditions used in this study.

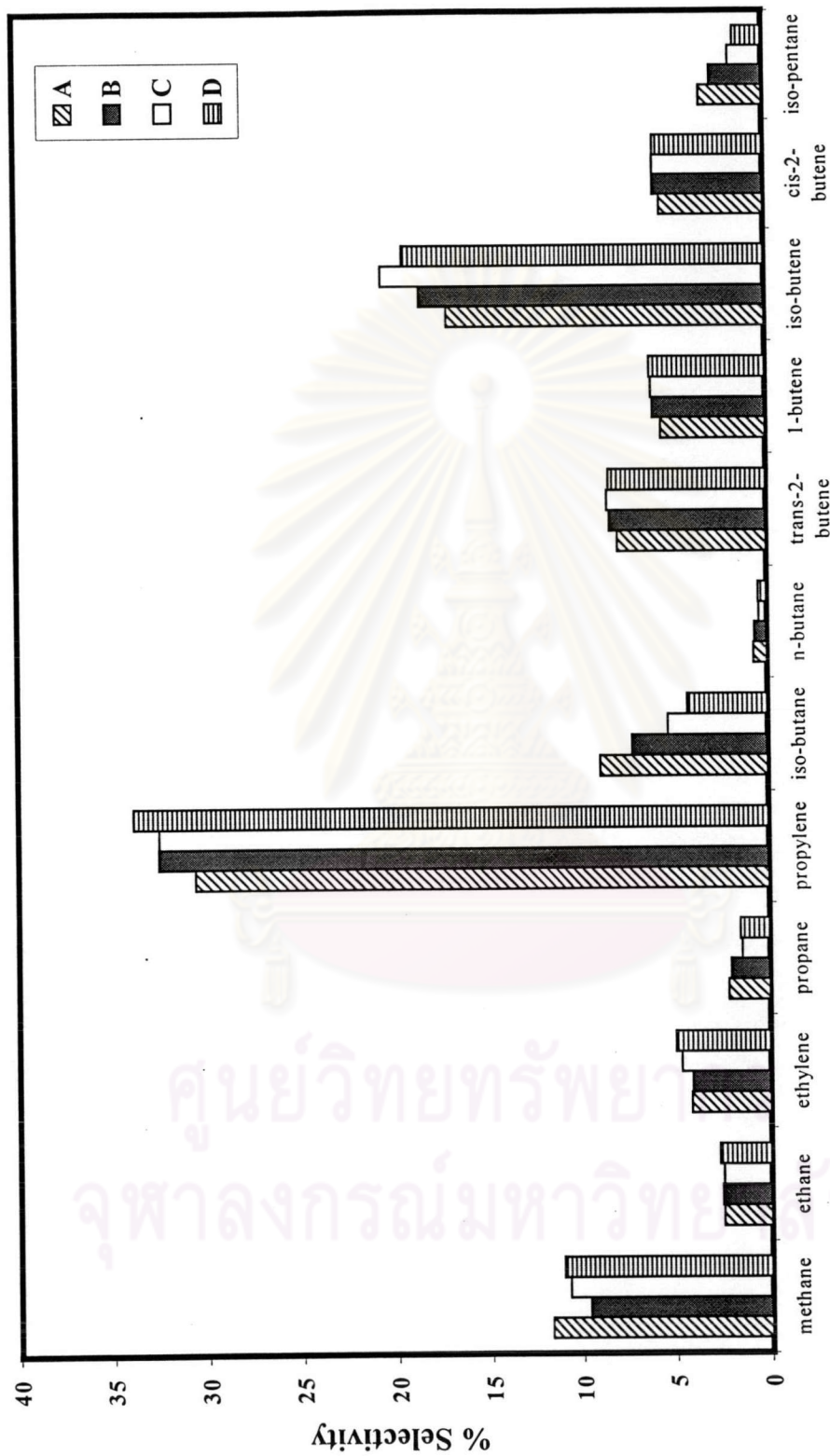


Figure 4.11 Composition of gaseous products from the catalytic degradation of polypropylene over the Al-MCM-41 catalysts with different Si/Al ratios (A) 20; (B) 40; (C) 60; (D) 80 at 550°C.

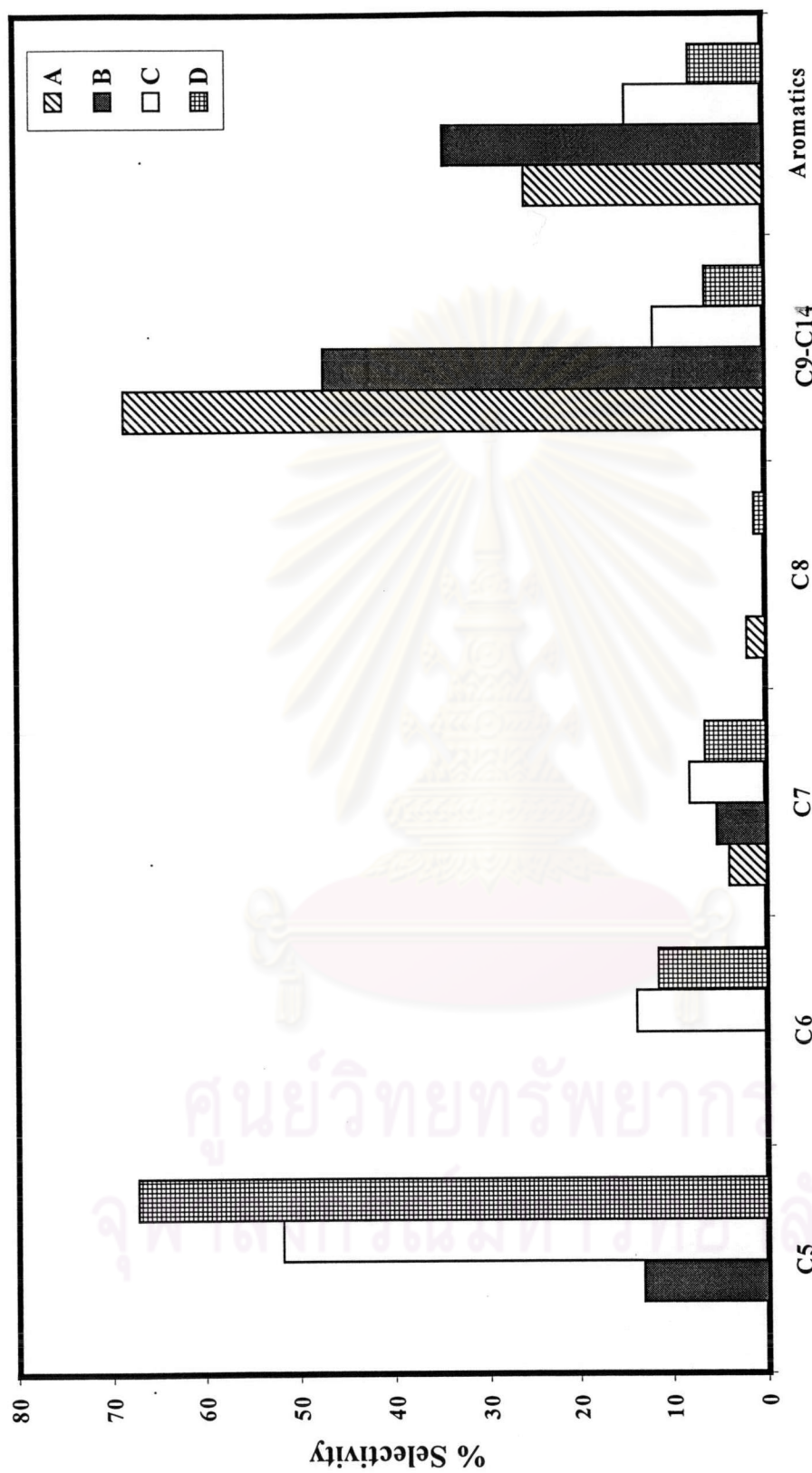


Figure 4.12 Yield of volatile liquid products in the catalytic degradation of polypropylene over the Al-MCM-41 with various Si/Al ratios (A) 20; (B) 40; (C) 60; (D) 80 at 550°C.

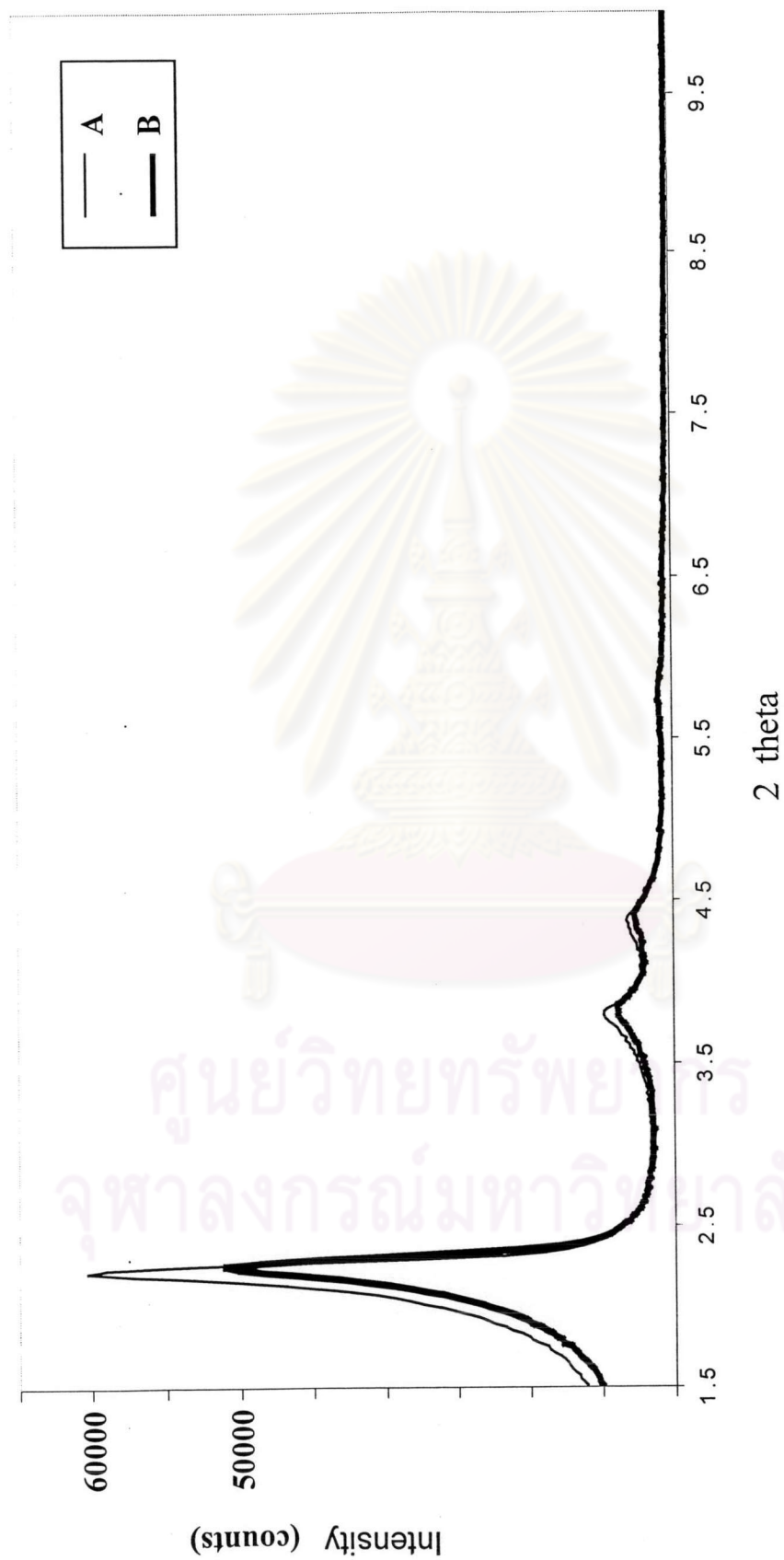


Figure 4.13 XRD patterns of the freshly calcined unused (A) and the regenerated (B) catalyst samples.

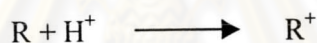


#### 4.5 Proposed Mechanism for Catalytic Cracking of Polypropylene over Al-MCM-41

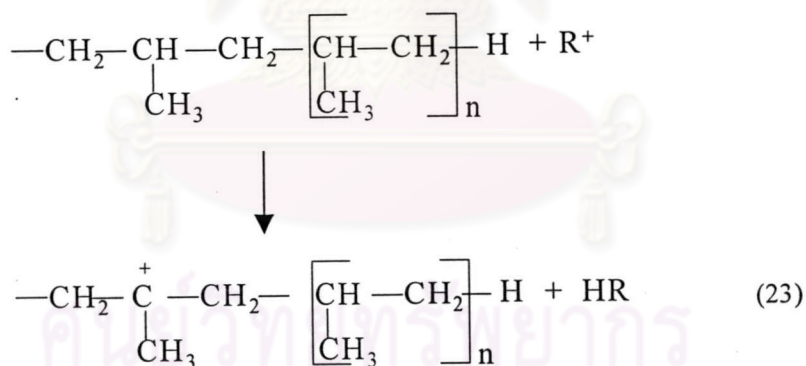
A mechanism for the catalytic degradation of polypropylene using Al-MCM-41 as catalyst is believed to be similar to that proposed by Ishihara et al.<sup>74</sup> The mechanism is proposed as follows :

##### 4.5.1 Mechanism of Oligomer Formation

Molecular weight reduction is first initiated by attack of low-molecular-weight carbonium ions,  $R^+$ , on hydrogen atoms attached to the tertiary carbon atoms of the polypropylene backbone chains (Equation 22). These ions are produced by protonation of volatile olefinic products present in the polymer as impurities. Generally, impurities are produced during oxidation by exposure to daylight and thermal degradation in extruders. The initiation reaction is as follows :

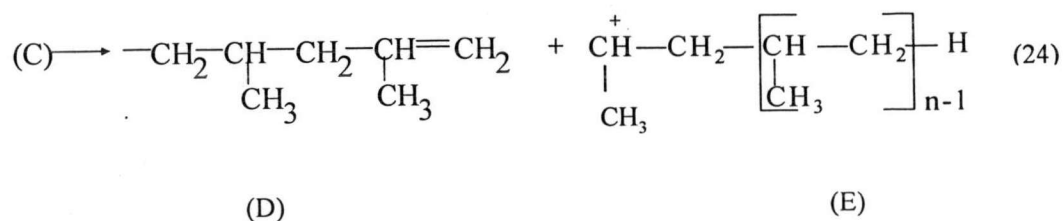


where R stands for volatile olefinic products. Then  $R^+$  can react further (22)

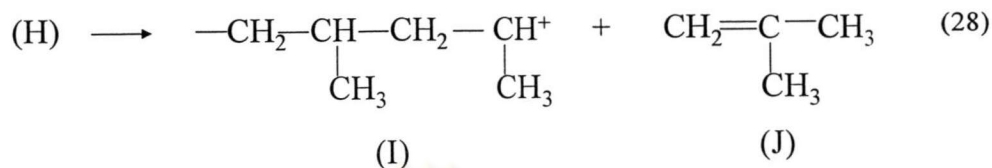
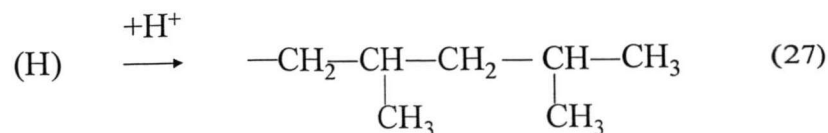


(C)

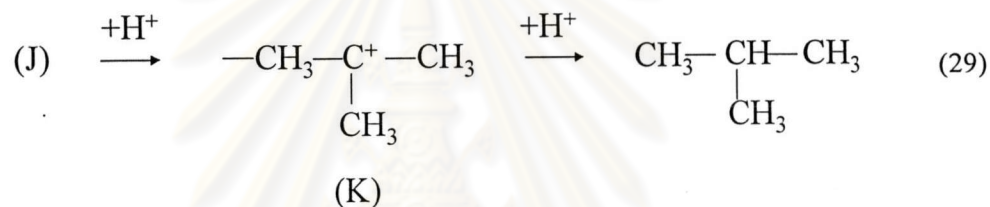
$\beta$ -Scission of on-chain carbonium ions (C) occurs to produce chain-ends (D) and (E) :





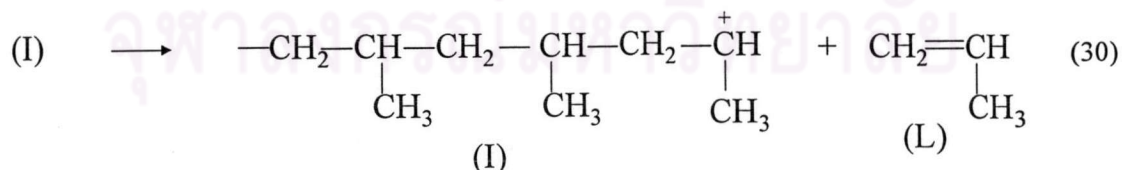


Chain-ends (I) and isobutene (J) are produced according to Equation (28). Isobutene (J) produces isobutane by hydrogenation as follows:

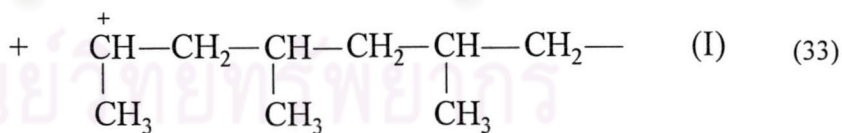
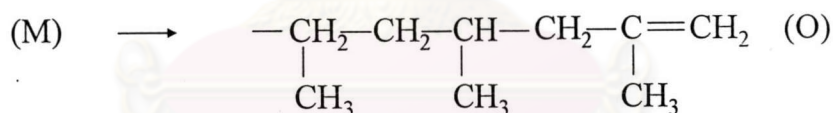
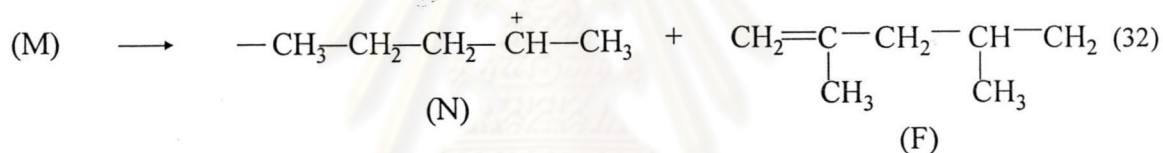
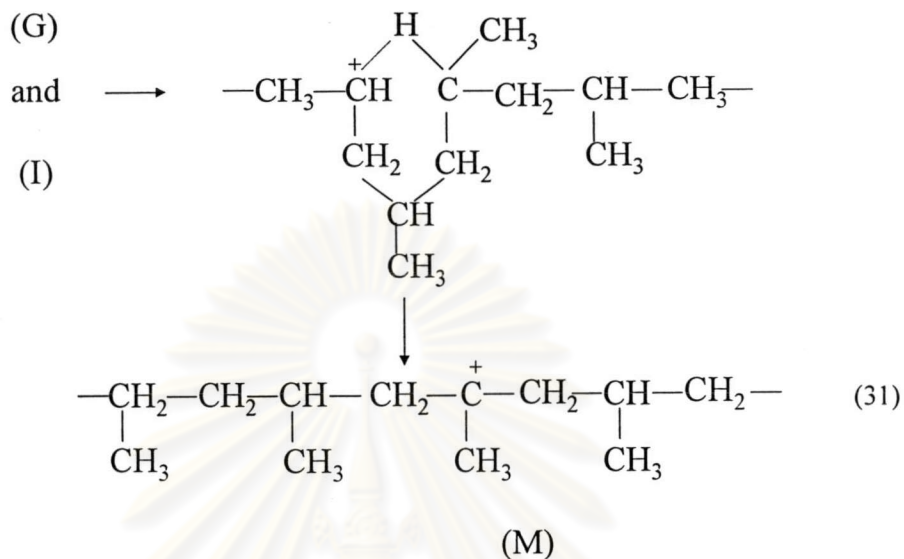


Carbonium ion (K) also attack the on-chain tertiary hydrogen atoms of the oligomer and liquid fractions, leading again to the production of on-chain tertiary carbonium ions. The gas fraction may be produced by decomposition of ions (G), (H), and (I).

The C<sub>4</sub> and C<sub>5</sub> fractions, which are the main components of gas cannot be produced by the direct β-scission of ions (G) and (H). Only the C<sub>3</sub> fraction may be produced via β-scission. β-scission of ions (I) requires a higher activation energy (190kJ mol<sup>-1</sup>) than isomerization (63 kJ mol<sup>-1</sup>) and thus occurs at a high temperature:



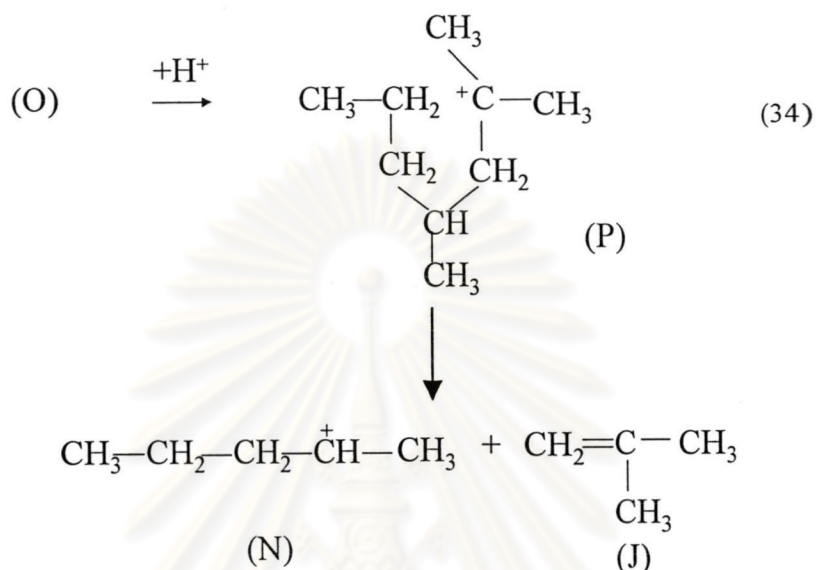
The propylene yield increased at high temperature and ion (I) is more easily stabilized by isomerization. Possible reaction steps for isomerization are as follows:



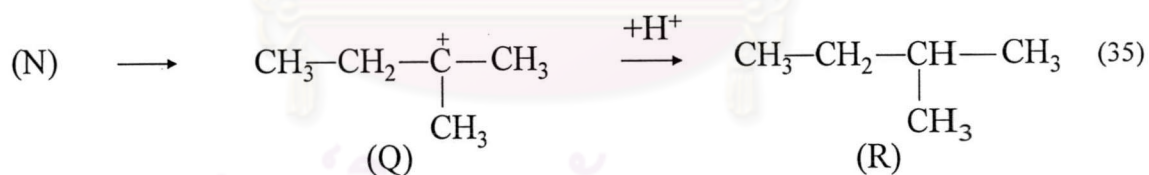
The isomerization of ions (G) and (I) proceeds by intramolecular rearrangement via a six-membered transition state to inner tertiary carbon atoms (back biting reaction). Ions (M) are stabilized by Equations (32) and (33). In the case of Equation (32), there is no gas formation from the chain-end olefins formed; consequently only the yield of the C<sub>5</sub> fraction should be important. The experiment results do not



support the existence of Equation (32). The reactions usually proceed to produce more stable products, and the process that mainly occurs is Equation (33). The C<sub>9</sub> fraction was the main product in the liquid fraction. Fraction (O) produces reaction intermediate (P) by protonation and then undergoes β-scission as follows:



Isopentane is thus produced with a high yield from isopentyl carbonium ions as shown in Equation (35). A small amount of n-pentane was produced by hydride ion addition to ion (N)



No isopentene could be detected. The main products of catalytic decomposition of polypropylene are isobutane and isopentane at low reaction temperature. At high temperature, Equation (30) occurs to produce propylene. The catalytic gasification of polypropylene proceeds primarily by means of the following steps: polymer → degraded polymer → oligomer → liquid (gasification precursor, e.g. C<sub>9</sub> fraction) → gas.