

## CHAPTER V

### RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided into three sections. First, synthesis and characterizations of beta zeolite synthesized by the dry gel conversion were presented in section 5.1. The powder was analyzed by using XRD, XRF, BET surface area, SEM and  $^{27}\text{Al}$  NMR. Second, catalytic behavior of beta zeolite is synthesized by the dry gel technique on the methanol conversion are explained in section 5.2. Third, the advantages for synthesis of beta zeolite by dry gel conversion are showed in section 5.3.

#### 5.1 Synthesis and Characterizations of beta zeolite by Dry Gel Conversion

##### 5.1.1 Effect of the water content in the reaction system

The effect of the amount of water using in the reaction system on the characteristics of beta zeolite by dry gel conversion were studied. The molar ratio of starting materials was  $\text{SiO}_2$ :  $0.01\text{Al}_2\text{O}_3$ :  $0.1\text{Na}_2\text{O}$ :  $0.37\text{TEAOH}$  and the reaction temperature were kept constant at  $175^\circ\text{C}$  for 24 h [5,6].

The X-ray diffraction patterns of the as-synthesized products prepared with various water contents (5, 10, 20, 30, 50 ml) are shown in Figure 5.2. The XRD patterns of commercial beta zeolite were showed for comparison as shown in Figure 5.1. The XRD patterns of beta zeolite indicate two main peaks at  $2\theta$  as  $7.8^\circ$  and  $22.4^\circ$ . This is a unique characteristic of beta zeolite in agreement with several works [42]. This approach used for characterization the type of crystals zeolite by comparing with the data of powder diffraction file [3], XRD pattern was specified for each crystal.

Beta zeolite was obtained directly from dry gel conversion with various water contents. The crystallinity of product increased corresponding to the increasing of water from 5 to 10 ml. However, after the water contents increased to 20, 30 and

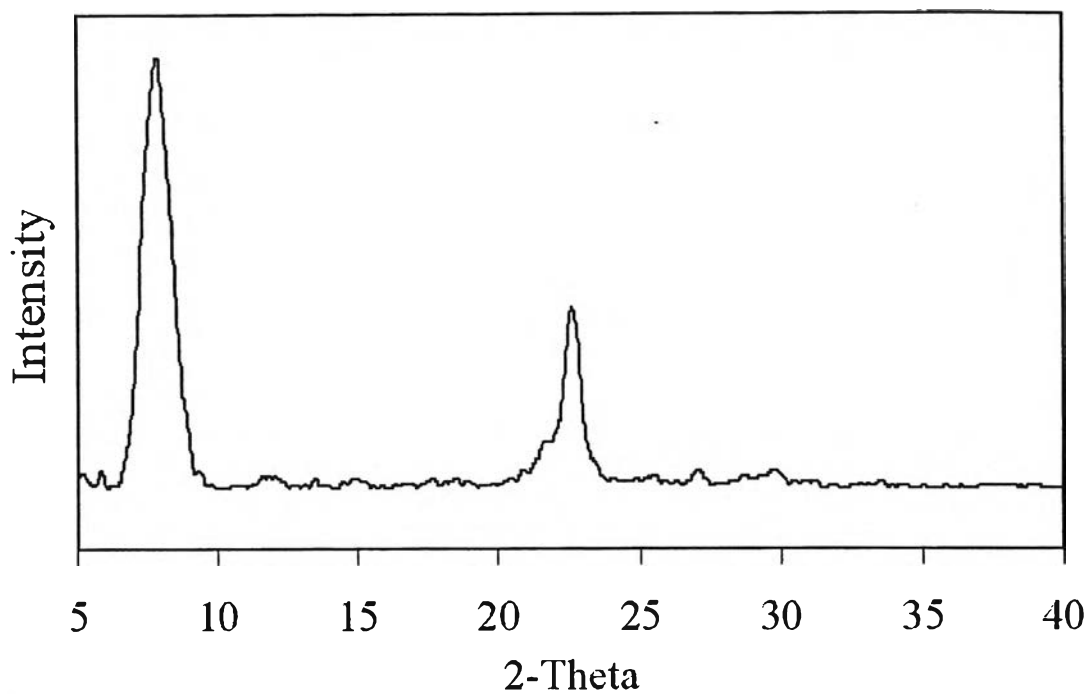
50 ml. the crystallinity decreased distinctly. It suggests that the amorphous phase was obtained and contaminated in the sample after the increasing of water content. The XRD patterns clearly shows the fact that the water content has a strong impact on the formation of beta zeolite synthesized by the dry gel method in agreement with the observation reported by Rao and Matsukata for Ti-BEA synthesis [77].

Provided that the vapor pressure of pure water in a singular system is merely considered, the calculated via the van der waals equation, a mass of water higher than 5.2 g in the autoclave 1,000 ml causes the presence of a liquid phase during the dry-gel conversion process at the 175°C [78]. However, this water amount to gives always amorphous and the calculated values are for lower than the water amount actually needed [20].

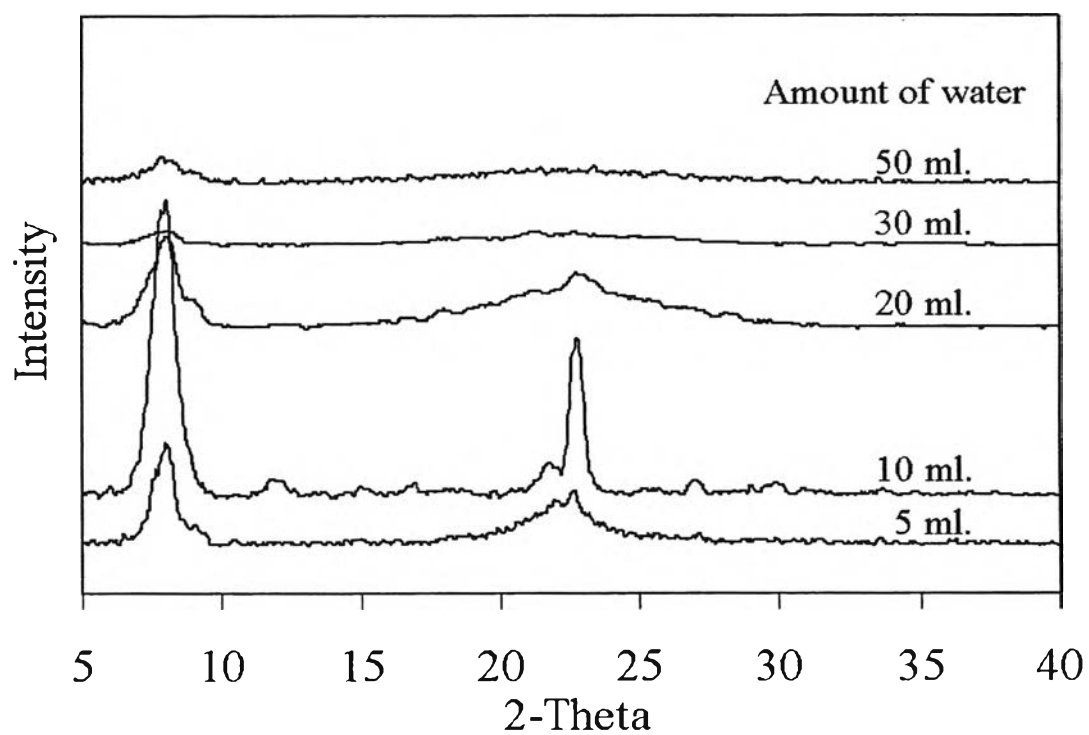
There are possible reasons responsible for these results due to the sealed autoclave contains at least 4 kinds of volatile components such as air, water, triethylamine and ethylene coming from TEAOH decomposition, among which triethylamine can dissolve into water. In this case the actual vapor pressure of water will reduce and the dissolution of triethylamine further affects the crystallization [20]. Hence, the presence of water is a prerequisite for the successful crystallization of beta zeolite using dry gel conversion. This finding is at some variance to the dry gel conversion process leading to the pure product, where vapor pressure of water in the range of the saturation pressure was sufficient to obtain materials with a high quality [19,20].

Matsukata et al. [19] have been reported that the requirement of an appropriate the water content exceeding the exact amount to keep the saturated vapor pressure suggests that condensation of water would take place particularly in the pores of dry gel. One may consider that the dry gel conversion method is a hydrothermal synthetic method that is performed under extremely dense conditions. However, this idea cannot explain the result that beta zeolite was not formed in the presence of a large excess water content. They have previously been reported [6] that in as-made beta zeolite,  $\text{TEA}^+$  cations are occluded and stabilized by interacting with the beta zeolite framework by forming  $\text{Al-O}^- \text{TEA}^+$  bonds (decomposing above 327°C) and

Si-O<sup>δ-</sup> TEA<sup>+</sup> bonds (decomposing above 177°C). Their conclusion, TEA<sup>+</sup> cations in a dry gel are forced to interact with (alumino)siliceous species in the absence of a continuous phase of water. Therefore, one may be expected regarding zeolite-forming reaction require water content that in the large excess water content of an appropriate the water content, the template cations would escape from the dry gel into the aqueous phase and then its degradation would take place when water condenses in the dry gel in large excess and forms a continuous phase and may be interfere in Al-O<sup>-</sup> TEA<sup>+</sup> bonds and Si-O<sup>δ-</sup> TEA<sup>+</sup> bonds due to OH<sup>-</sup> and H<sup>+</sup> of H<sub>2</sub>O decomposition in large excess water content. These are probably the resulted that can not the formation of beta zeolite.



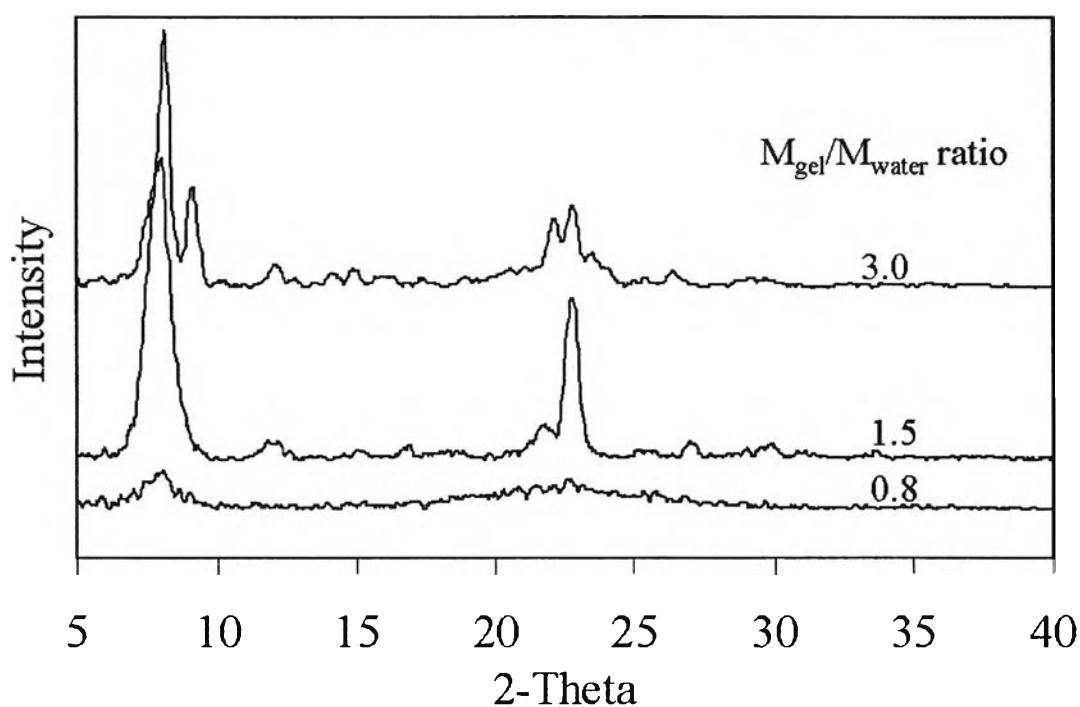
**Figure 5.1** XRD pattern of commercial beta zeolite



**Figure 5.2** XRD patterns of beta zeolite synthesized by dry gel conversion with difference amounts of water as source of steam

### 5.1.2 Effect of the dry gel mass

Figure 5.3 shows the XRD patterns of products prepared via dry gel conversion with the variation of dry gel masses. According to these XRD patterns, it is clear that highly crystalline beta zeolite was obtained with  $M_{\text{gel}} / M_{\text{water}}$  ratio of 1.5. A decrease of the mass of dry gel ( $M_{\text{gel}} / M_{\text{water}} = 0.8$ ) produced an amorphous phase and increasing of the mass of dry gel ( $M_{\text{gel}} / M_{\text{water}} = 3.0$ ) led to the formation of ZSM-12 as impurity. Transformation of beta zeolite into ZSM-12, OU-1 or ZSM-5 during the dry gel conversion has been reported previously [79,80].



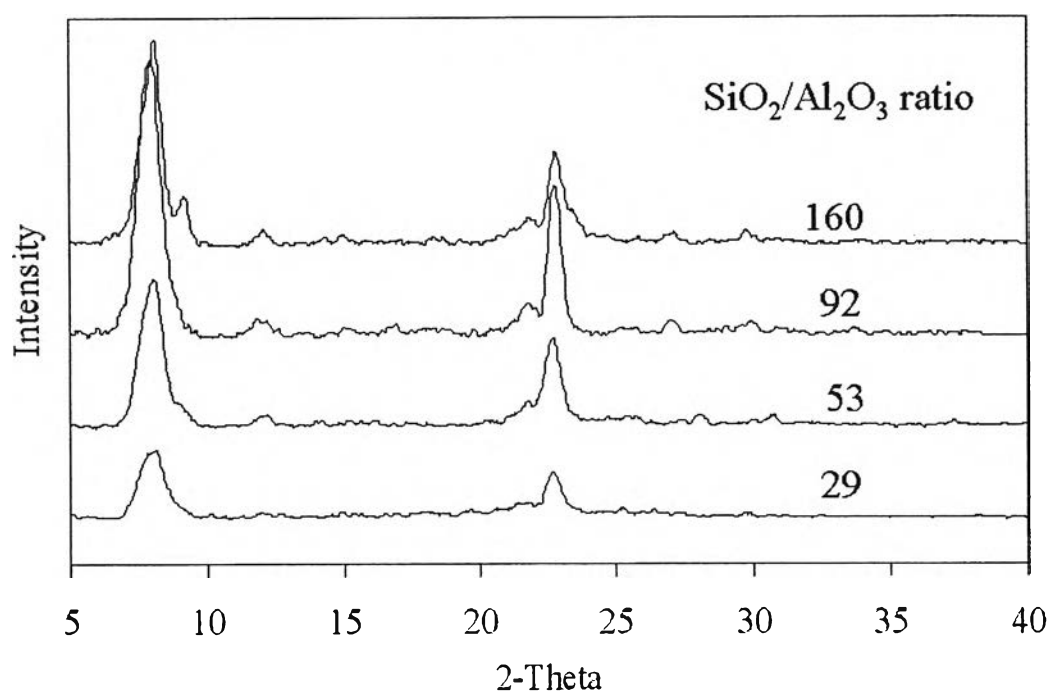
**Figure 5.3** XRD patterns of beta zeolite synthesized by dry gel conversion with difference  $M_{\text{gel}}/M_{\text{water}}$  mass ratios

### 5.1.3 Effect of silica to alumina ratio

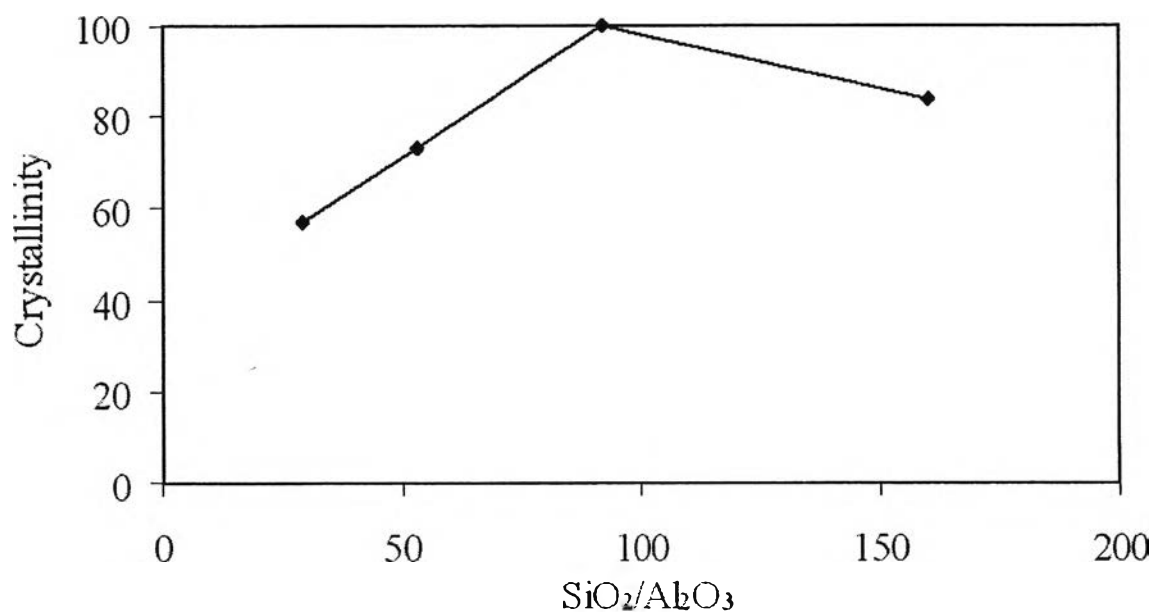
Figure 5.4 shows the XRD patterns of beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29, 53, 92 and 160, when water content and  $M_{\text{gel}}/M_{\text{water}}$  mass ratios was 10 and 1.5, respectively. The product with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29, 53 and 92 was beta zeolite. However, the contamination of ZSM-12 was observed in the product with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 160, which the XRD peak of ZSM-12 appear at  $2\theta = 7.4, 8.2, 21.2,$  and  $24.9$  [3]. A similar result has been reported by Matsulata et al. [19] for conversion of dry gel to microporous crystals in gas phase. Which  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increased, beta zeolite being to transform to ZSM-12 and undesired product after prolonged crystallization time.

The relative crystallinity of products calculated from the peak intensity at  $22.4^\circ$ . From most of literature reviewed [28,52,81], the peak intensity at  $22.4^\circ$  was extensively accepted to be a main characteristic peak of beta zeolite and this peak was therefore chosen as a calculated peak. (For calculation see appendix A-2). The results of calculation are shown in Figure 5.5. The relative crystallinity of beta zeolite increased corresponding to the increasing of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 29 to 92 and decreased to 80 at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 160 as result of impurity formation. Kasture et al. [82] have reported that it is impossible to make highly crystalline beta zeollite at low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio with hydrothermal synthesis.





**Figure 5.4** XRD patterns of beta zeolite synthesized by dry gel conversion with difference SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios



**Figure 5.5** Relationship between percent relative crystallinity and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of beta zeolite synthesized by dry gel conversion

## 5.1.4 Physical and Chemical properties of beta zeolite with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios

### 5.1.4.1 Chemical composition of thus-obtained products

The chemical composition was calculated by XRF analysis, and confirms the silica and alumina in the synthesized beta zeolite are summarized in Table 5.1.

**Table 5.1** Chemical composition of beta zeolites

$\text{SiO}_2/\text{Al}_2\text{O}_3$	
Gel	Product
30	29
60	53
100	92
200	160

### 5.1.4.2 The physical properties of thus-obtained products

The physical properties of beta zeolite are summarized in Table 5.2. The BET surface area increased from 251 to 475  $\text{m}^2/\text{g}$  and the relative crystallinity increased from 57 to 100% corresponding to the increasing of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 29 to 92. However, after the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  increased to 160, the BET surface area and the relative crystallinity of products decreased. This can be explained by the formation of ZSM-12 contamination.



**Table 5.2 The physical properties of beta zeolites.**

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> product	BET (m <sup>2</sup> /g)	%Relative crystallinity*	Particle size (μm)	Phase
29	251	57	0.09	Beta zeolite
53	363	73	0.12	Beta zeolite
92	475	100	0.26	Beta zeolite
160	341	84	0.1-2.1	Beta+ZSM-12

\* Based on intensity of XRD peak at  $2\theta = 22.4^\circ$  taking sample SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 100 as the reference

### 5.1.3.3 Morphology of thus-obtained products

Figure 5.5 shows typical scanning electron micrographs (SEM) images for beta zeolite synthesized by dry gel conversion with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 29, 53, 92 and 160, which can be seen in Figure 5.5, 5.6, 5.7 and 5.8 respectively. The average particle sizes of product are summarized in Table 5.2. The average particle size was calculated from

$$\text{Average particle size} = \frac{\sum (n_i d_i^3)}{\sum (n_i d_i^2)}$$

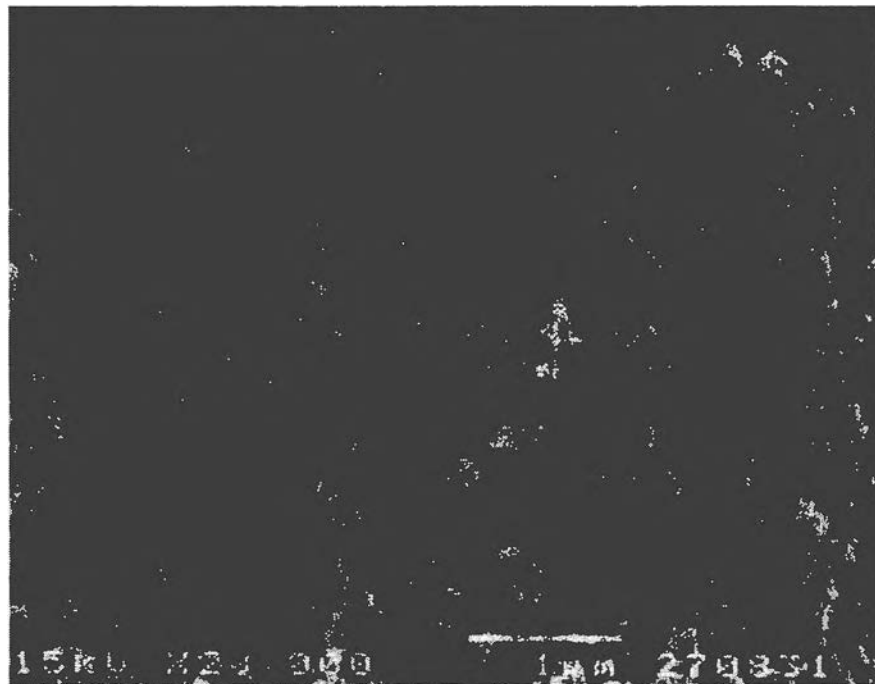
When  $n_i$  is number of particle at  $d_i$   
 $d_i$  is diameter of particle  $i$

The particle size of product and particle size of products increased from 0.09 to 0.26 μm corresponding to the increasing of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio from 29 to 92. This trend has also been reported in hydrothermal synthesis of beta zeolite [33]. While, the particle size decreased after the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio increased to 160, which due to the formation of ZSM-12. The morphology of thus-obtained products synthesized by dry gel conversion was square bipyramid with shown in Figure 5.5-5.7. From SEM image in Figure 5.8, two types of particle were observed. The square bipyramid particles due to the beta zeolite and large polyhedral with smooth surface

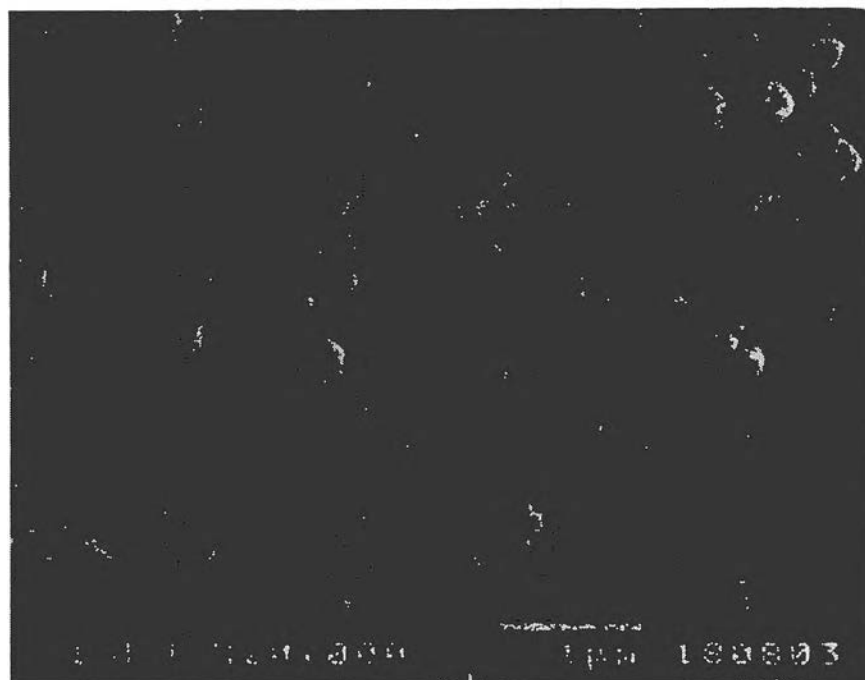
particle were presented. These large particles might be assigned to the ZSM-12 particles.



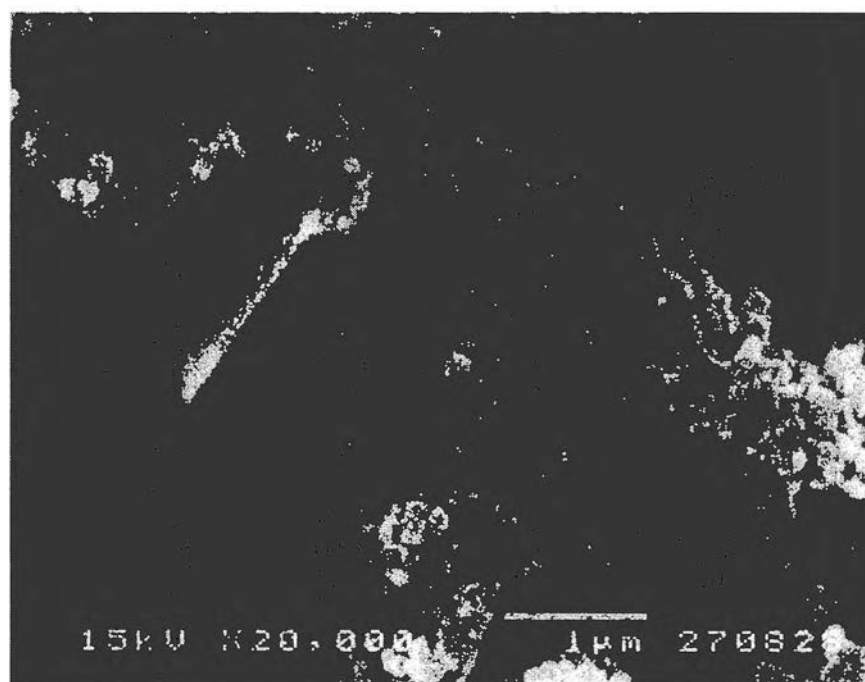
**Figure 5.6** Scanning electron micrographs of beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29



**Figure 5.7** Scanning electron micrographs of beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 53



**Figure 5.8** Scanning electron micrographs of beta zeolite synthesized by dry gel conversion with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 92

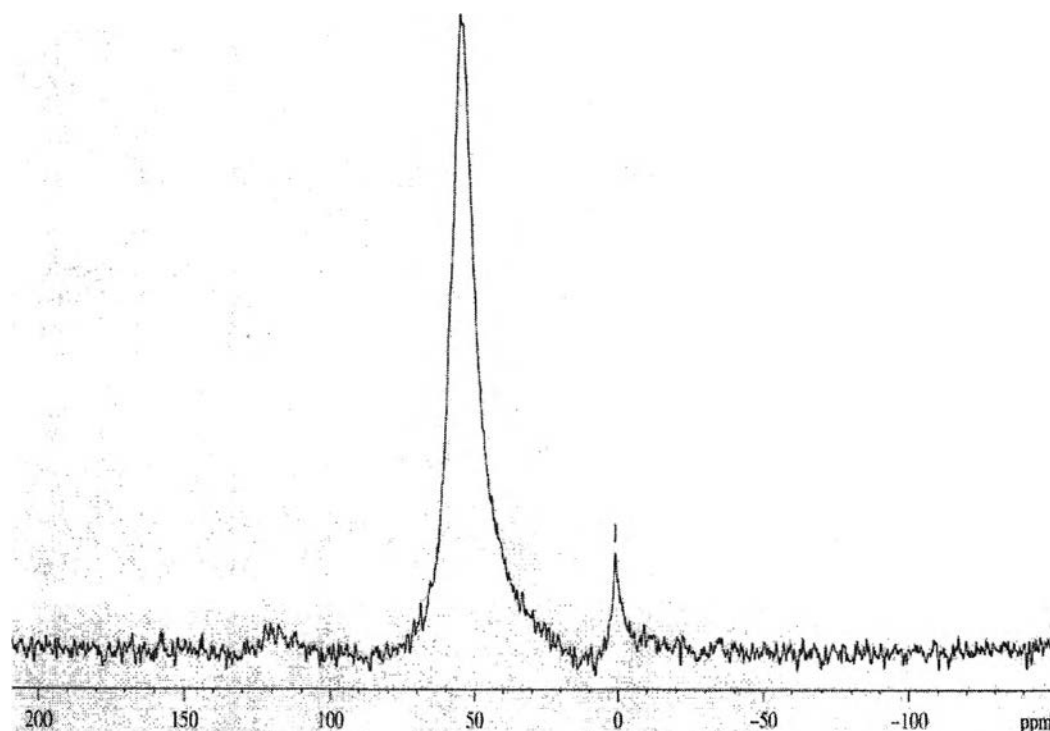


**Figure 5.9** Scanning electron micrographs of beta zeolite synthesized by dry gel conversion with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 160

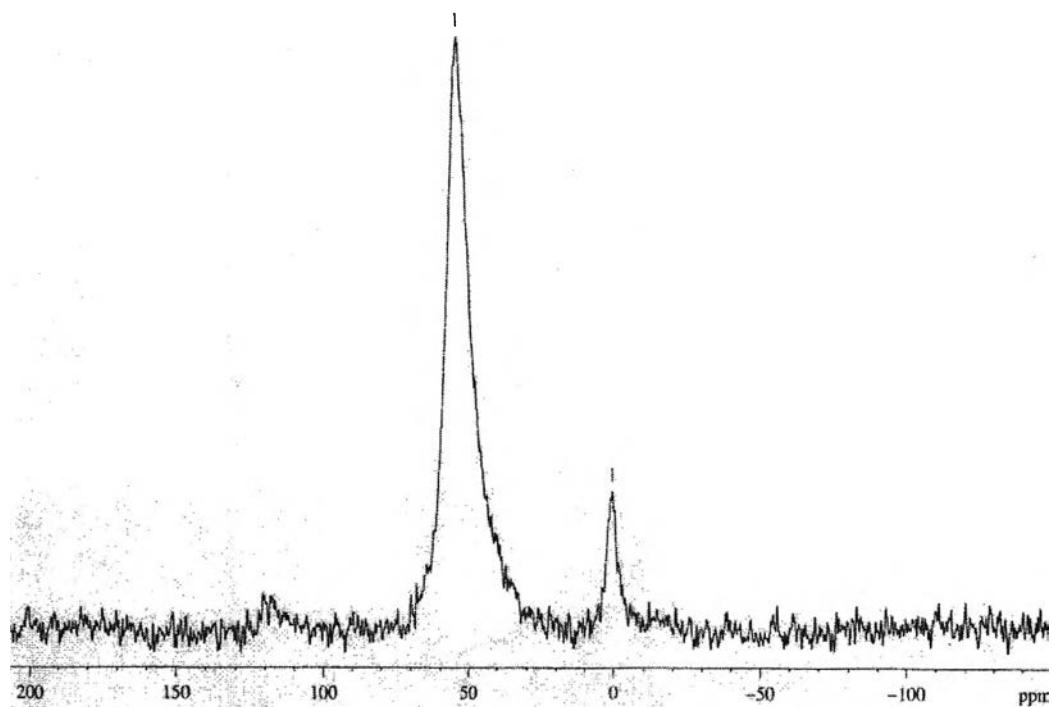
#### 5.1.3.4 Framework Al content by $^{27}\text{Al}$ MAS NMR Spectra

Measuring  $^{27}\text{Al}$  MAS NMR spectra provides information about the environment of the aluminum atoms in the zeolite sample. Al-tetrahedral presented in the zeolite framework ( $\text{Al}(\text{OSi})_4$ ), displays the NMR feature at  $\sim 53$  ppm. On the other hand, extra-framework aluminum (EFAI) species are usually octahedral coordinates which appear signal at a chemical shift of  $\sim 0$  ppm.

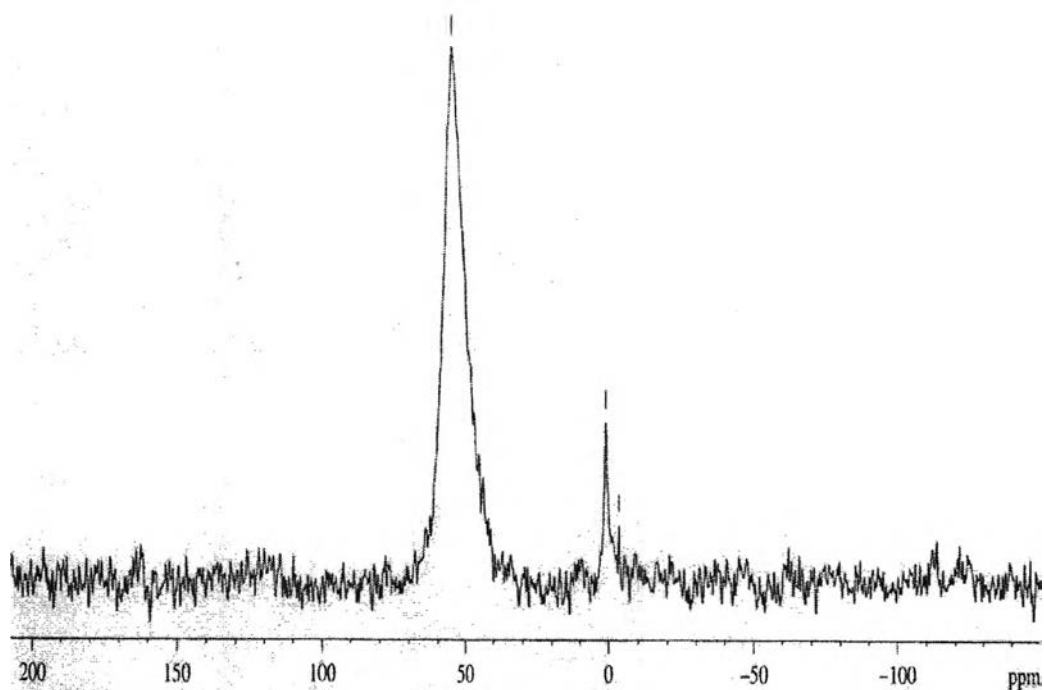
The  $^{27}\text{Al}$  MAS NMR spectra for beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29, 53, 92 and 160 are shown in Figure 5.10 – Figure 5.13. The product of beta zeolite shows a strong peak at ca. 53 ppm due to tetrahedral coordinated framework Al and a very weak peak at ca. 0 ppm due to octahedral coordinated extra framework Al (EFAI). The octahedral aluminum species in the products were formed during the transformation process from as-synthesized to H-form that is after calcinations a small part of aluminum atoms are released from the zeolite framework. [60].



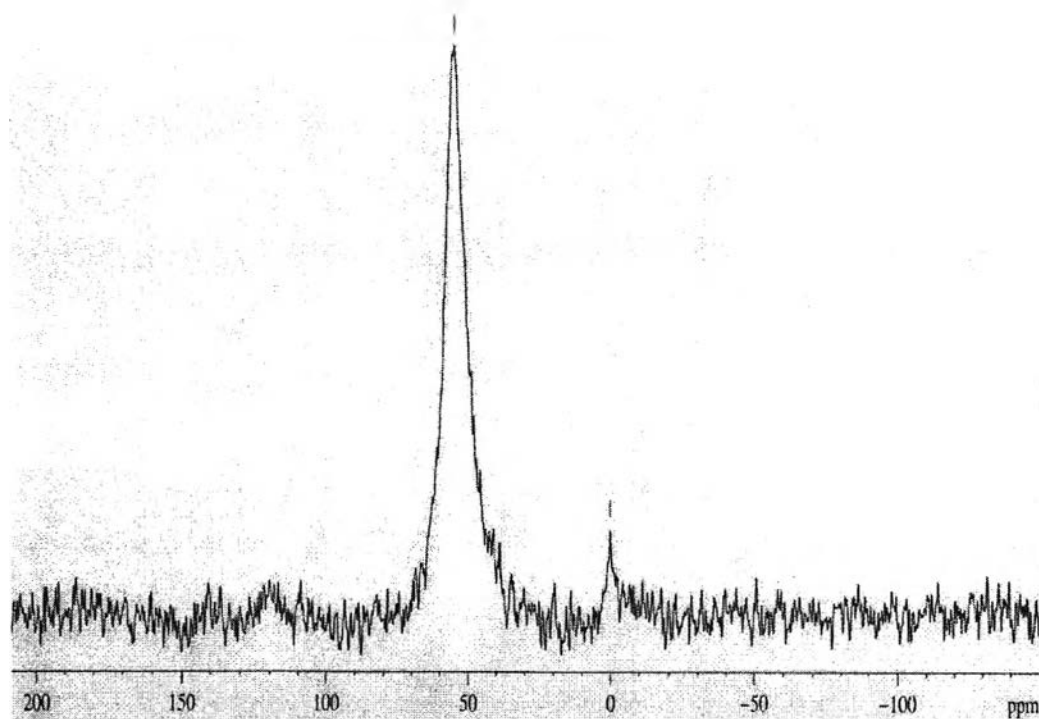
**Figure 5.10**  $^{27}\text{Al}$  MAS NMR spectra of H-zeolite beta synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29



**Figure 5.11**  $^{27}\text{Al}$  MAS NMR spectra of H- beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 53



**Figure 5.12**  $^{27}\text{Al}$  MAS NMR spectra of H- beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 92



**Figure 5.13**  $^{27}\text{Al}$  MAS NMR spectra of H- beta zeolite synthesized by dry gel conversion with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 160

## 5.2 Reaction Testing

The catalytic performance of the beta zeolite synthesized by dry gel conversion was tested in the reaction of methanol conversion. The methanol conversion obtained at a constant space velocity and a constant temperature for the four samples as a function of time on stream is shown in Figure 5.14, each sample was investigated on stream for the period of 8 hour. As can be seen, after 5 hours of operations, all the samples reached the steady-state level of activity. The catalytic activity of the beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 92 is higher compared to other.

As expected, for beta zeolite prepared by dry gel conversion the catalytic activity is increased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. The increase in the methanol conversion corresponding to the increasing of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 29 to 92 and decreased at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 160, it suggests that the resulted of crystallinity of beta zeolite synthesized by dry gel conversion. Kasture et al. [82] have reported that the increase in the benzene conversion with the increase in crystallinity of beta zeolite may partly be associated with increasing in the number of acidic sites, pore volume, and surface area. Yoo and Smirniotis [83] have reported that zeolites where the aluminum distribution in the pores varies locally and/or the pore network is not uniform (small pores are connected with relatively large voids) they believe that the acid site strength can very significantly with respect to the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and dealumination methods. Toophorm et al. [84] synthesized polycrystalline zeolite beta using hydrothermal method. They found that the change of the small particle size was easily occurred than that of the large one and the higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of beta zeolite more stable on dealumination under hyderthermal treatment.

The product distributions of beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 29 for three different time on stream are shown in Figure 5.15. It was found that, initially, conversion of methanol was 83.40%, iso-butane was main product. After the reaction was prolonged the conversion dropped to 63.44% and the main product changed to be ethylene and propylene. This resulted due to the fact that, when the reaction was prolonged, water was produced as the by-product of the reaction. Which it was damaged the structure of beta zeolte by dealumination process. The structure collapse

was affected on the decreasing bronsted acid site. Normally, the formation of iso-butane should occurred by two bronsted acid site. When the decreasing of bronsted acid site, the balance selectivity decreased corresponding to the decreased of acid site. After the reaction at 300 minute time on stream, conversion dropped to 61.22% and reached the steady-state level of activity, the main product changed to be methane. An increase in the methane selectivity is probably due to the decrease of the amount of the strong acid sites. For the beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 53 for three different time on stream are shown in Figure 5.16. It was found that, initially, conversion of methanol was 93.08%, iso-butane was main product. After the reaction was prolonged the conversion dropped to 86.39% and the main product changed to be ethylene and propylene. After the reaction at 300 minute time on stream, conversion dropped to 77.40% and reached the steady-state level of activity, the main product changed to be methane. And the beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 92 for three different time on stream are shown in Figure 5.17. It was found that similar the product distribution was obtained from beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 29 and 92, initially, conversion of methanol was 79.48%, iso-butane was main product. After the reaction was prolonged the conversion dropped to 74.12% and the main product changed to be ethylene and propylene. After the reaction at 300 minute time on stream, conversion dropped to 72.03% and reached the steady-state level of activity, the main product changed to be methane. However, beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 160 is shown in Figure 5.18. It was found that, initially, propylene was main product. After 120 minute on stream, iso-butane increased was obtained, which difference from the results of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 29, 53 and 92 due to structure of zeolte due to different of structure was obtained, it had impurity formation from the dry gel synthesis.



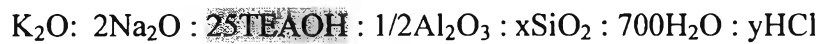
### 5.3 The advantages for synthesis of beta zeolite by dry gel conversion.

The advantages for synthesis of beta zeolite by dry gel conversion, when comparison between dry gel conversion and hydrothermal method will be showed as follows:

#### **Beta zeolite by hydrothermal method**

Aging time: 40 h.

Gel molar composition



#### **Beta zeolite by dry gel conversion method**

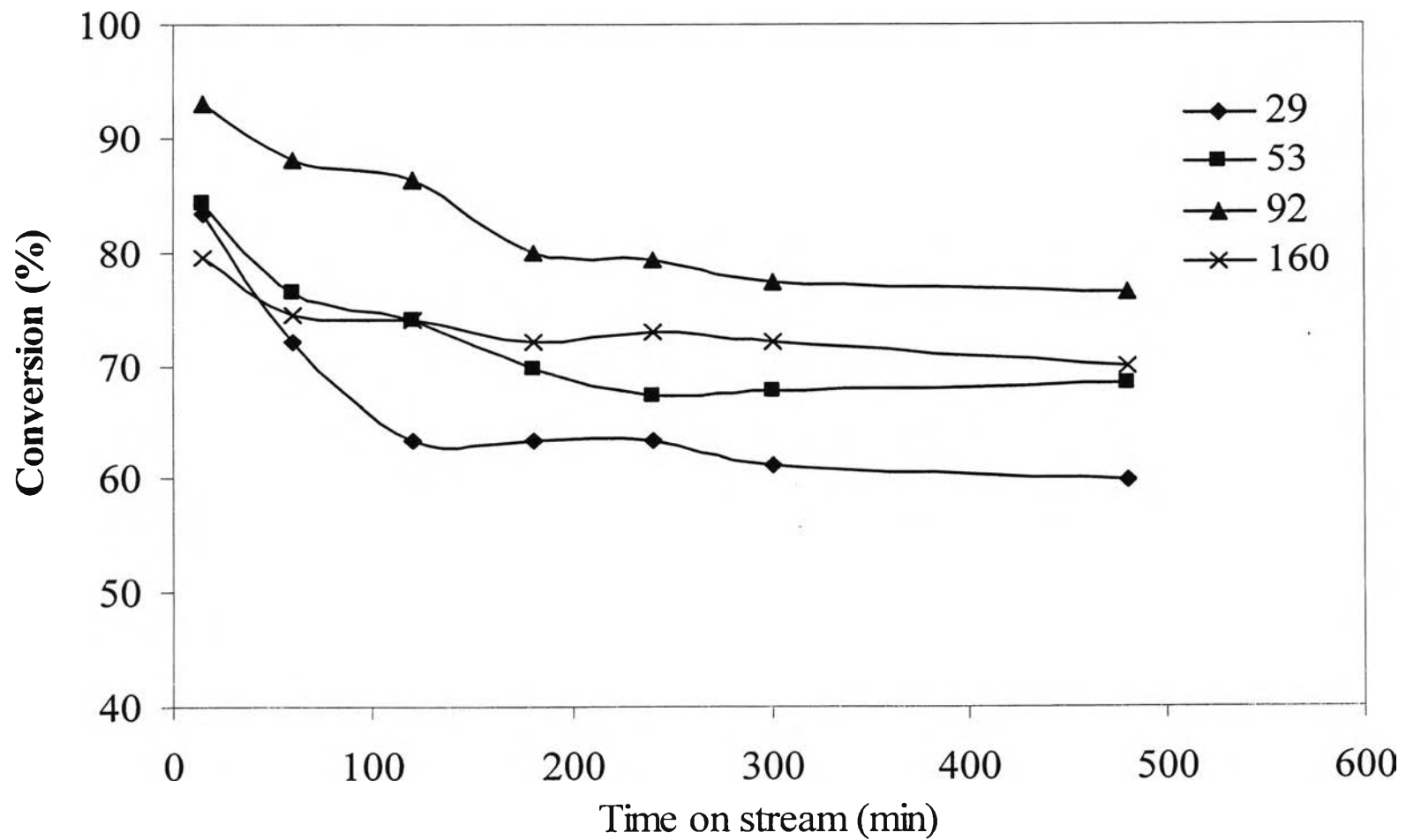
Aging time: 24 h.

Gel molar composition



Synthesis of beta zeolite by dry gel conversion method has the following advantages over the hydrothermal crystallization method;

1. Reduction of the consumption of expensive organic template.
2. Rapid crystallization.



**Figure 5.14** Methanol conversion time on stream on conversion of beta zeolite synthesized by dry gel conversion with difference SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios

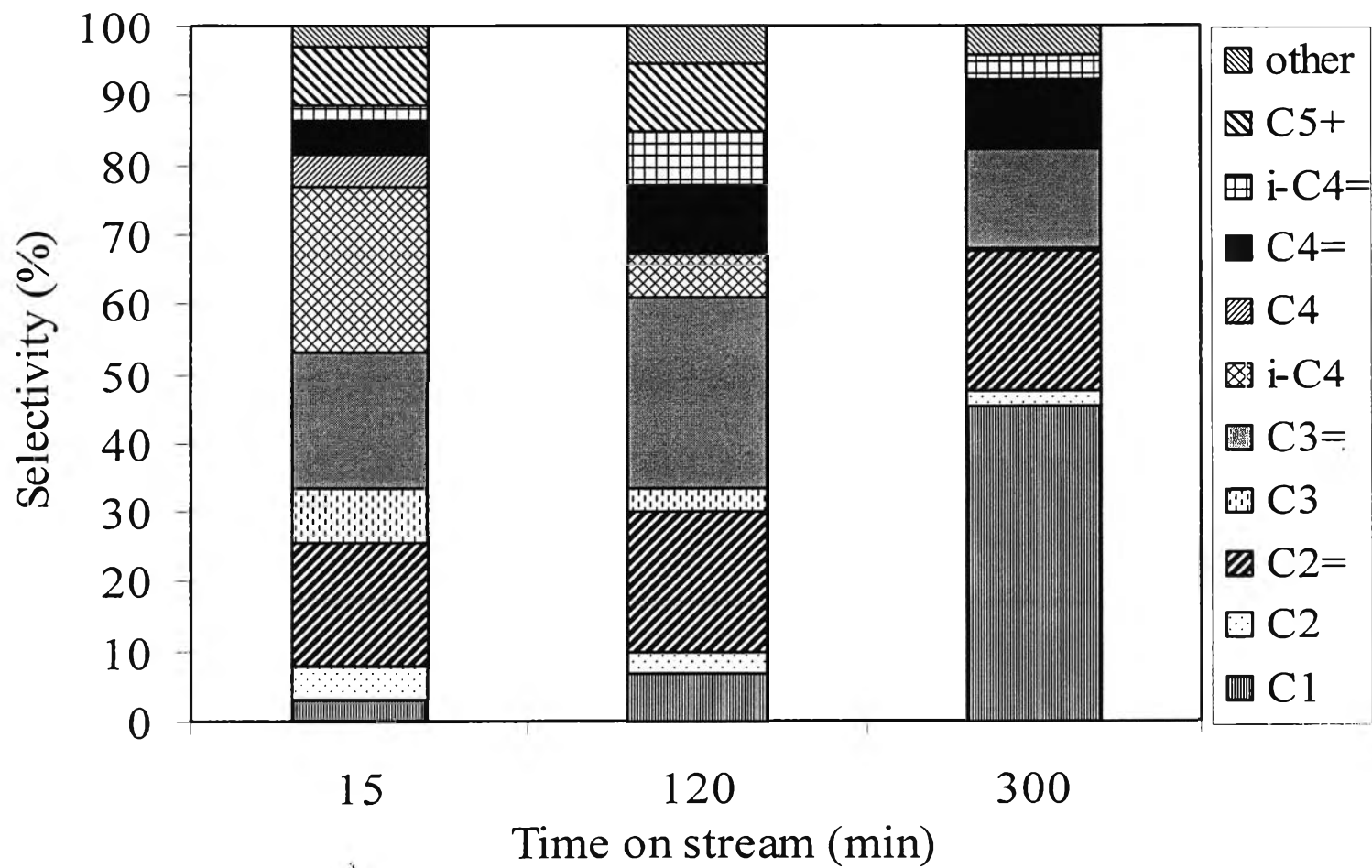
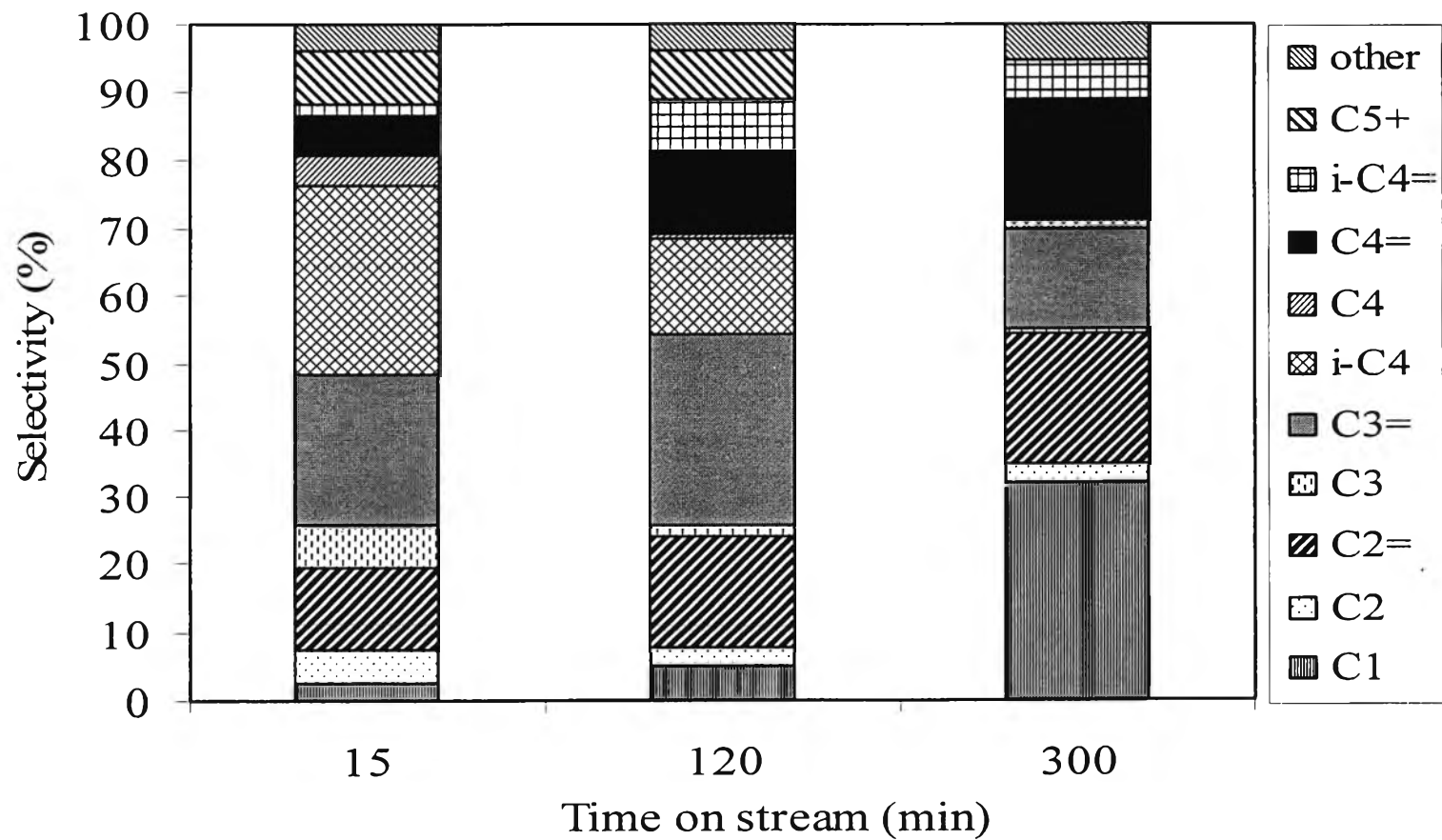
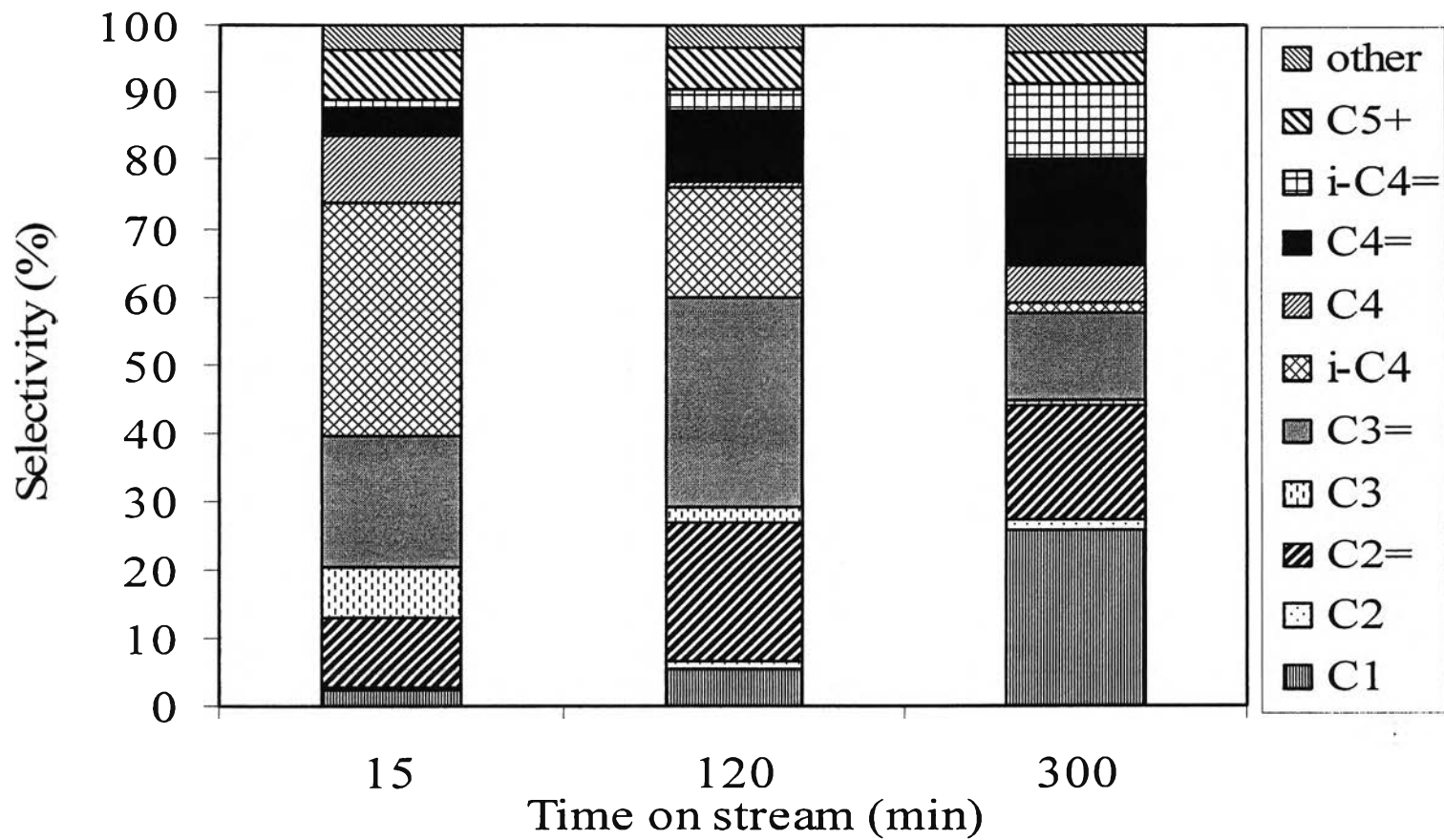


Figure 5.15 Selectivity of product distribution as a function of stream of beta zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 29



**Figure 5.16** Selectivity of product distribution as a function of stream of beta zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 53



**Figure 5.17** Selectivity of product distribution as a function of stream of beta zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 92

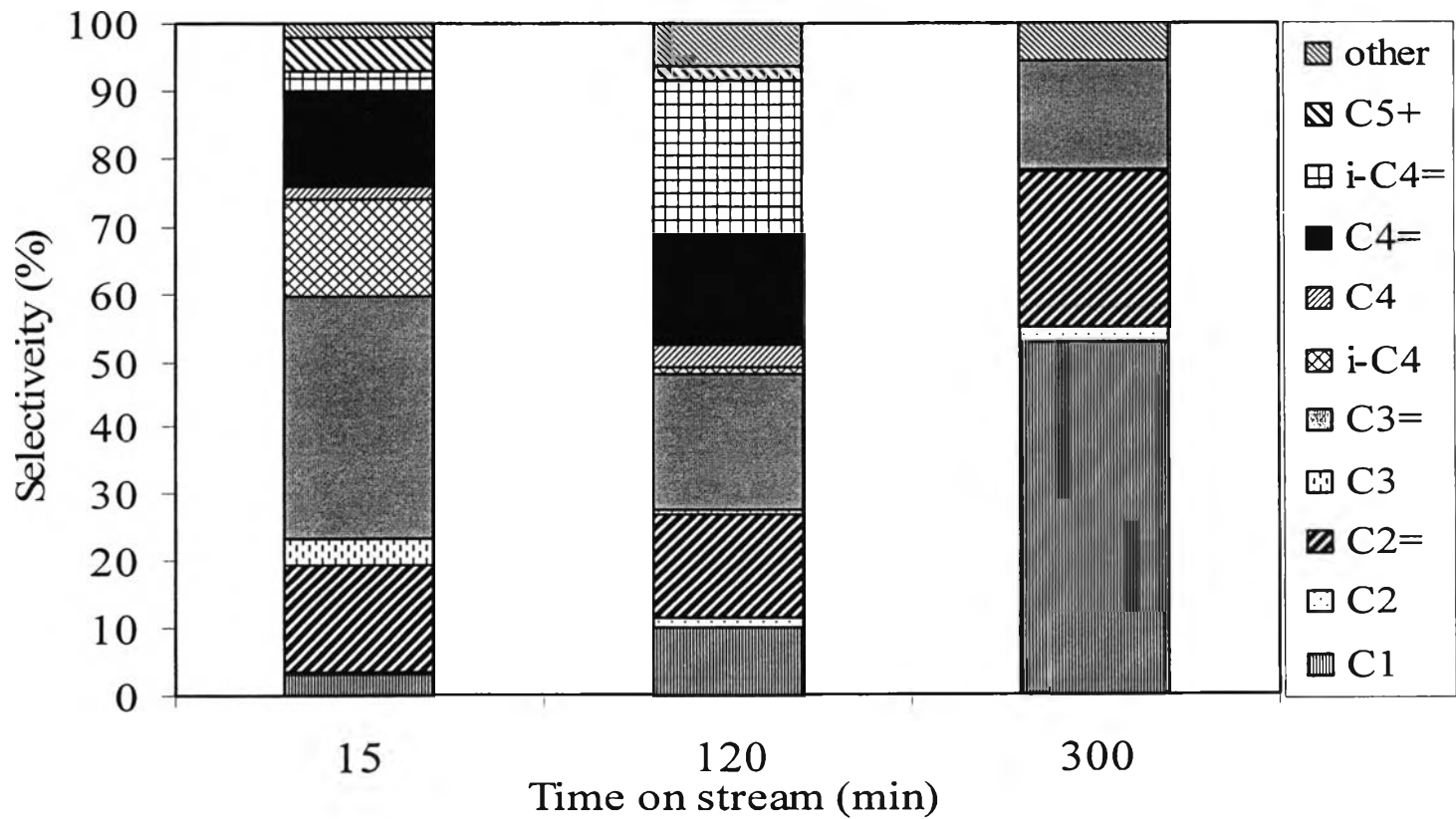


Figure 5.18 Selectivity of product distribution as a function of stream of beta zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 160