



CHAPTER IV

RESULTS AND DISCUSSION

As mentioned in Chapter III that the main factors which affect the characteristics of synthetic crystals were concentrated on the following aspects: 1. chemical compositions of crystals, 2. initial pressure for crystallization, 3. pH of mixing solution, 4. temperature and time in crystal synthesis, and 5. temperature and time in calcination process. The experimental results of these factors were discussed as follow.

4.1 The Chemical compositions of crystals

4.1.1 Characterizations of product crystals by crystallinity analysis.

The XRD patterns for pentasil zeolite from various Si/Al mole ratios at initial pressure of 3 kg/cm² (gauge) were shown in fig. 4.1.1. From each pattern, the d-value from Bragg's equation were calculated by choosing at least three point of the 2θ which have maximum intensity. These procedure used for characterization the type of zeolite crystal by comparing with the data of powder diffraction file in section 3.2.1, XRD-pattern was specified for each crystals. As for crystallinity, these also related to the intensity of major XRD-peaks for the amounts of sample, i.e. the higher in intensity of peaks, the more crystallinity (at 2θ = 23.3^o, 8^o, and 24^o). From fig. 4.1.1, at Si/Al mole ratio of 20, the XRD-signal just had developed to be peak. It illustrated that the crystallinity was very low (from intensity of XRD-peak) and not clear to specify the type of crystal. However at 32^o

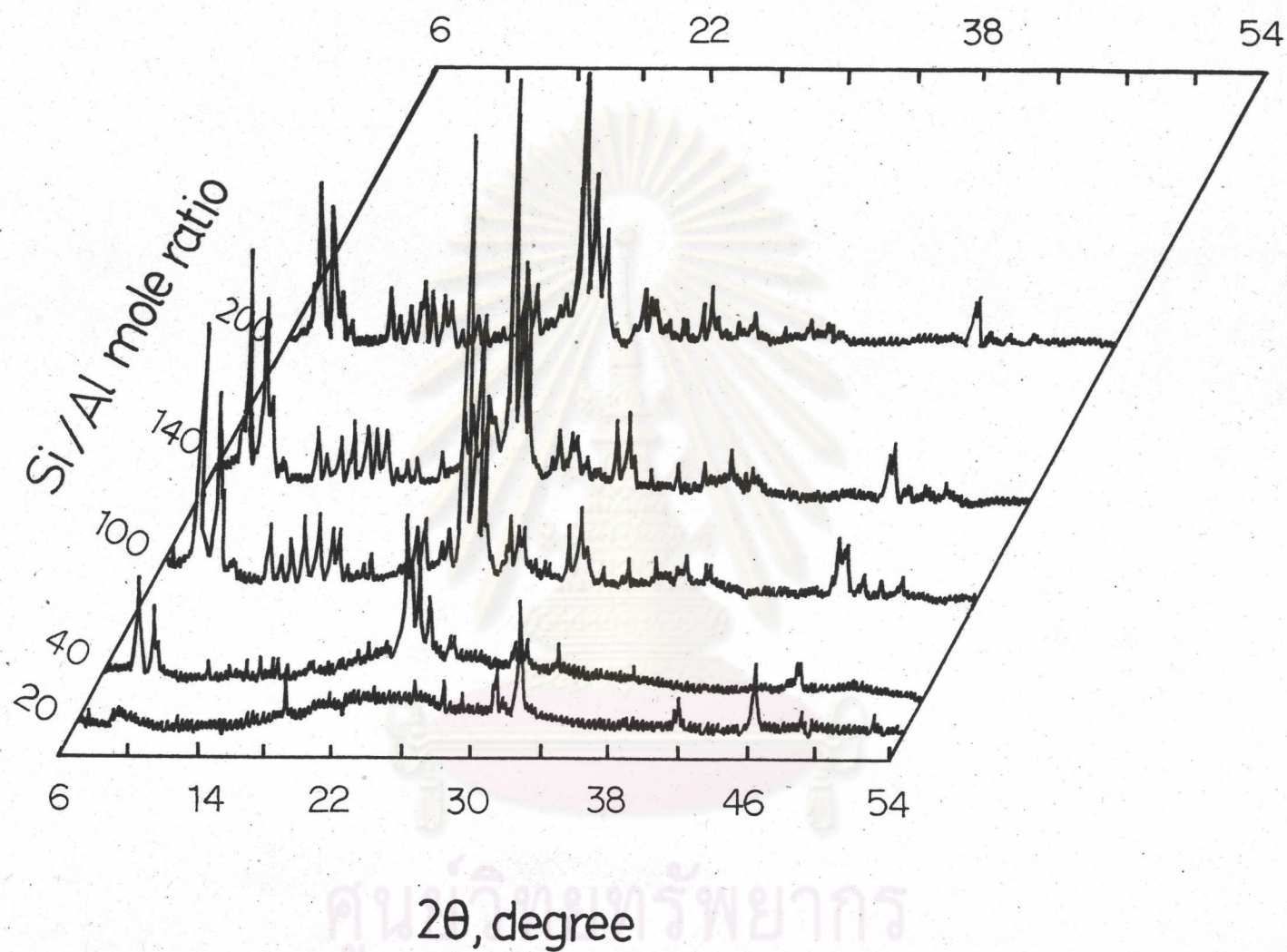


Figure 4.1.1 XRD patterns for pentasil zeolites from various Si/Al mole ratios at initial pressure of 3 kg/cm^2 (gauge)

of 20, there was a medium intensity peak which corresponded to the sodium chloride crystals those remain contaminated after washing step of crystal. The XRD-pattern of NaCl crystal was shown in fig. 4.1.2.

On the other hand the XRD-signal of Si/Al mole ratio 40 showed clear pattern of pentasil zeolite. After the calculation for d values from the 20 of three maximum peaks, the results indicated that the product crystal was ZSM-5 zeolite.

In addition to Si/Al mole ratios of 100, 140, and 200 the XRD-patterns were also similar to ZSM-5 type zeolite. Furthermore the crystallinity of product crystals at Si/Al mole ratio of 100, 140 and 200 were very high compared with Si/Al mole ratio of 20 and 40. The order of crystallinity for various Si/Al mole ratio was as the following

$$\text{Si/Al mole ratio} \quad 20 < 40 < 100 < 140 > 200$$

The results indicated that as for Si/Al mole ratio ranging from 20 and 200, the crystallinity of ZSM-5 zeolites were increased with increasing of Si/Al mole ratios and Si/Al mole ratio of 140, showed the the highest in this range.

4.1.2 External structure (Morphology) analysis by scanning electron microscope.

SEM-photomicrographs of Si/Al mole ratios of 20, 40, 100, and 140 were shown in figs. 4.1.3-4.1.6, respectively.

From fig.4.1.3, SEM-photomicrograph showed that the product crystals were amorphous forms, like granules of the the same size (about 1-2 μm). It was shown that there was no ZSM-5 crystal which had been developed in crystal synthesis at Si/Al mole ratio 20 and initial pressure 3 kg/cm^2 (gauge).

From fig.4.1.4, the product crystals contained amorphous forms and spherical forms of ZSM-5 zeolite which had the average size about 10 μm . Because at Si/Al mole ratio 40, ZSM-5 crystals had been

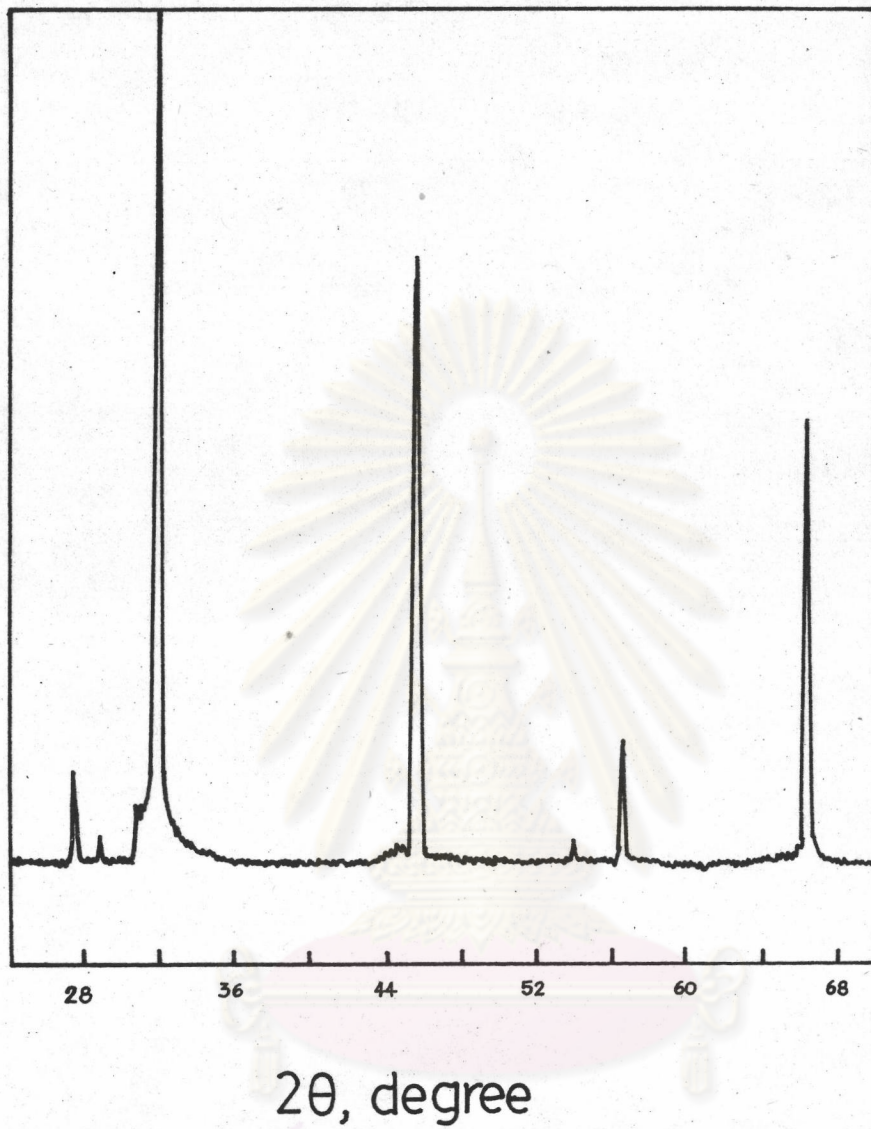


Figure 4.1.2 XRD patterns of sodium chloride crystal

developed about 60-70% of product crystal, this condition would be the optimum condition for zeolite synthesis.

For the SEM photomicrograph at Si/Al mole ratio of 100, in fig. 4.1.5, product crystals contained 70-80% of spherical formed ZSM-5 zeolite and impurity. The size of ZSM-5 crystals was about 7 μm , therefore, this condition was better than that at Si/Al mole ratio 40.

The SEM-photomicrograph of product crystal at Si/Al mole ratio 140 was shown in fig. 4.1.6. The results were the same as at Si/Al mole ratio 100 but percentage of ZSM-5 crystals were 75-85% of product crystals. When the results of SEM-photomicrographs were compared with each other, from various Si/Al mole ratio, and at initial pressure 3 kg/cm^2 (gauge), the most optimum Si/Al mole ratio for ZSM-5 synthesis was 140.

4.1.3 Functional group analysis

The Infrared spectra of zeolites at various Si/Al mole ratios were shown in fig. 4.1.7. At Si/Al mole ratio of 20 there were strong bands at 950-1,250 cm^{-1} which illustrated asymmetric stretching mode of T-O bond and at 420-500 cm^{-1} which illustrated bending mode of T-O bond in TO_4 tetrahedron framework. At 750-820 cm^{-1} , it was symmetric stretching band of external linkage modes.

at Si/Al mole ratio 40, the results were all the same as those at Si/Al mole ratio 20 except the stronger symmetric stretching band of external linkage modes and the appearance of double ring external linkages band at 500-650 cm^{-1} .

In the case of Si/Al mole ratio 100, bands of double ring and symmetric stretching of external linkages were stronger than those at Si/Al mole ratio 40 the other results were similar.

At Si/Al mole ratio 140, all the results were the same as those at Si/Al mole ratio 100 but the sizes of double ring and symmetric



Figure 4.1.3 SEM photomicrograph of product crystals at Si/Al mole ratio 20



Figure 4.1.4 SEM photomicrograph of product crystals at Si/Al mole ratio 40

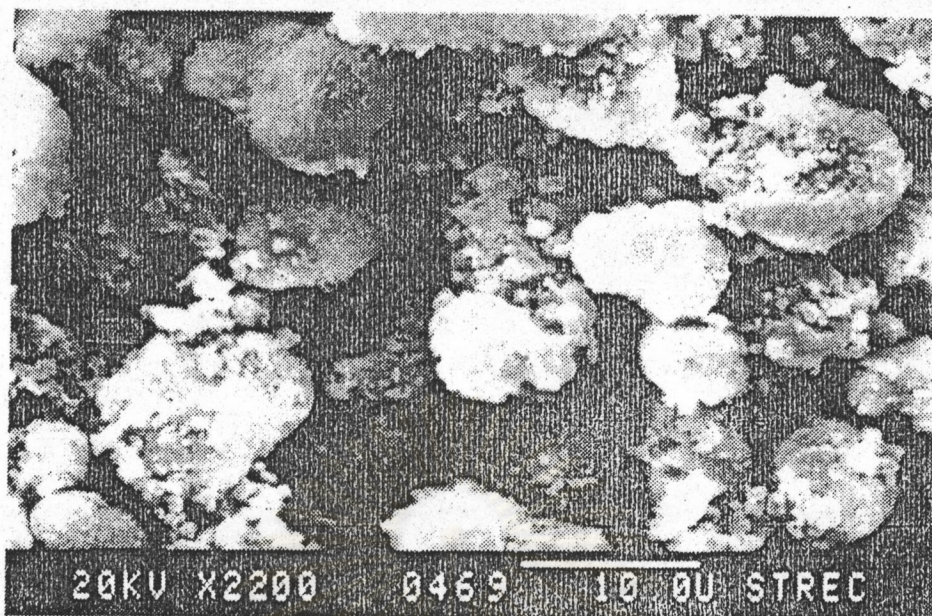


Figure 4.1.5 SEM photomicrograph of product crystals at Si/Al mole ratio 100

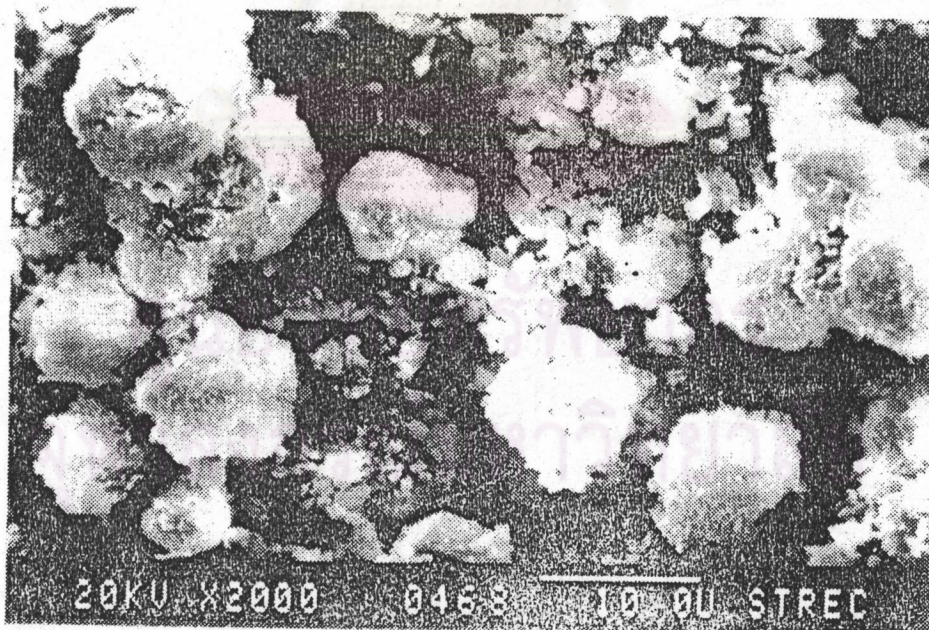


Figure 4.1.6 SEM photomicrograph of product crystals at Si/Al mole ratio 140

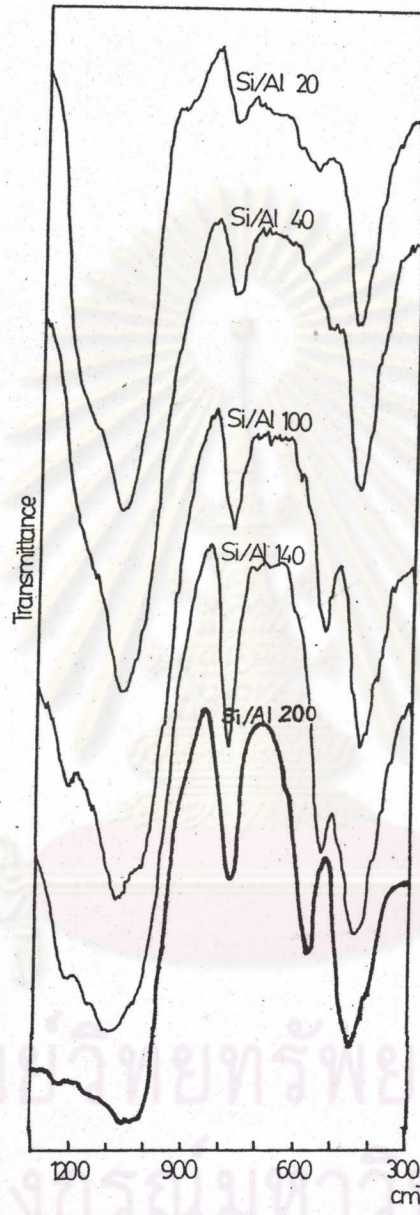


Figure 4.1.7 IR spectra of product crystals at various Si/Al mole ratio

stretching bands were the strongest when compared with the other conditions.

From all results mentioned above, it could be found that all of product crystals had TO_4 tetrahedron frameworks and when Si/Al mole ratio were increased from 20 to 140, band sizes of double ring and symmetric stretching of external linkages also were increased therefore, the structure of external linkages was more complete.

4.1.4 Chemical element analysis

In the study of the effects of crystal chemical compositions, the results from Atomic Absorption Spectroscopy AA were shown in table 4.1, No. 4.1.4-4.5.4, respectively. These real Si/Al mole ratios showed the quantities of Silicon and Aluminum in the product crystals.

From No.4.1.4, when Si/Al mole ratios were increased, the real Si/Al mole ratios were increased too but in the lower rate than Si/Al mole ratios and these results indicated that higher Si/Al mole ratios made higher quantities of aluminum which incorporated in framework structure.

When all of the results mentioned above were compiled together, there showed that the most optimum Si/Al mole ratio in ZSM-5 zeolites synthesis in the range of 20 and 140 was 140.

4.2 Initial pressures in the crystallization period.

4.2.1 Characterization of product crystals by crystallinity analysis.

Figures 4.2.1 and 4.2.2 showed the x-ray diffraction patterns for pentasil zeolites for various Si/Al mole ratios at initial pressure 1 and 5 kg/cm² (gauge), respectively. From fig. 4.2.1 at Si/Al mole ratio 20, the XRD-signal was very few developed to be peak, the crystallinity being very low, therefore, it was difficult to specify the

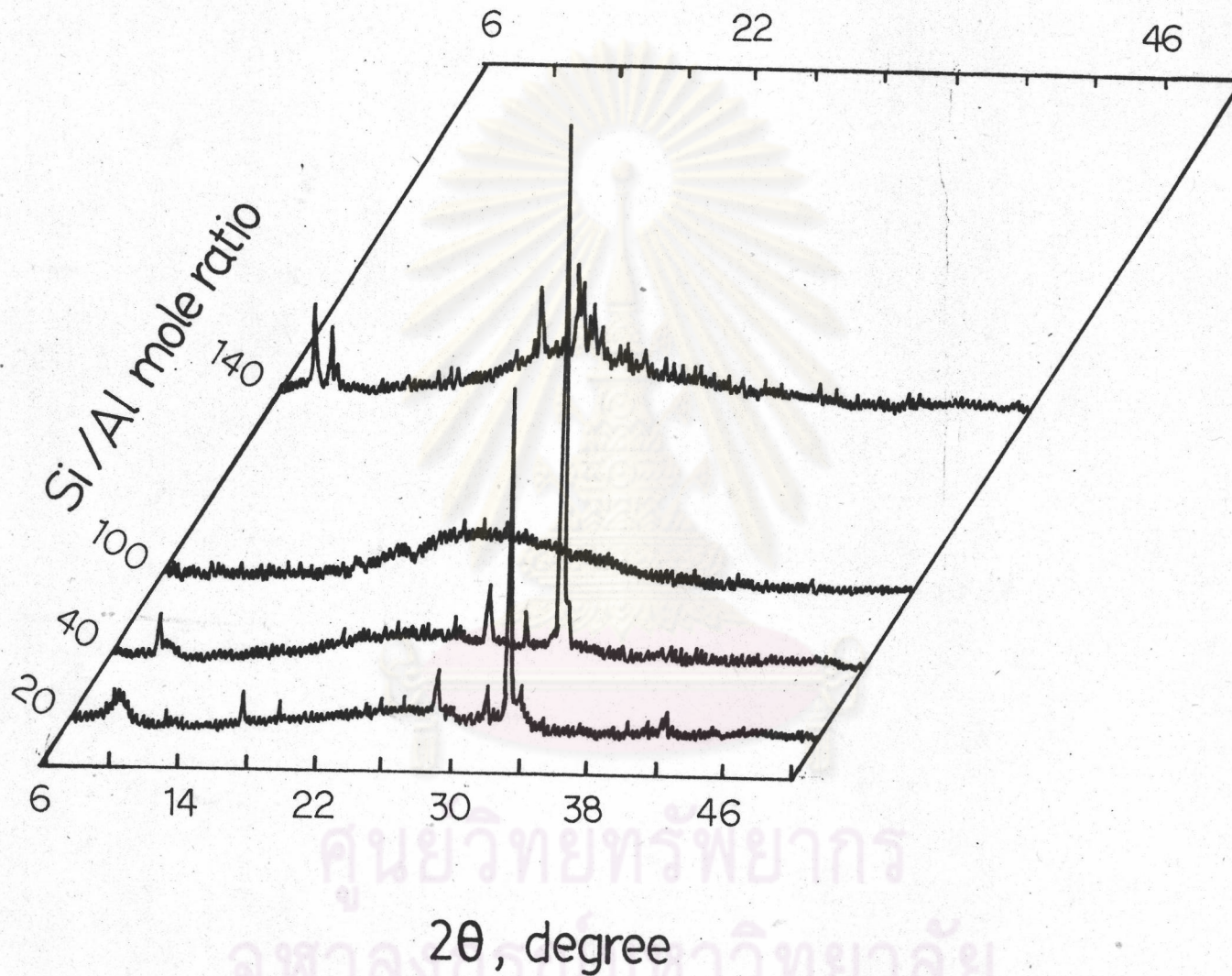


Figure 4.2.1 XRD patterns of pentasil zeolites from various Si/Al mole ratios at initial pressure 1 kg/cm^2 (gauge)

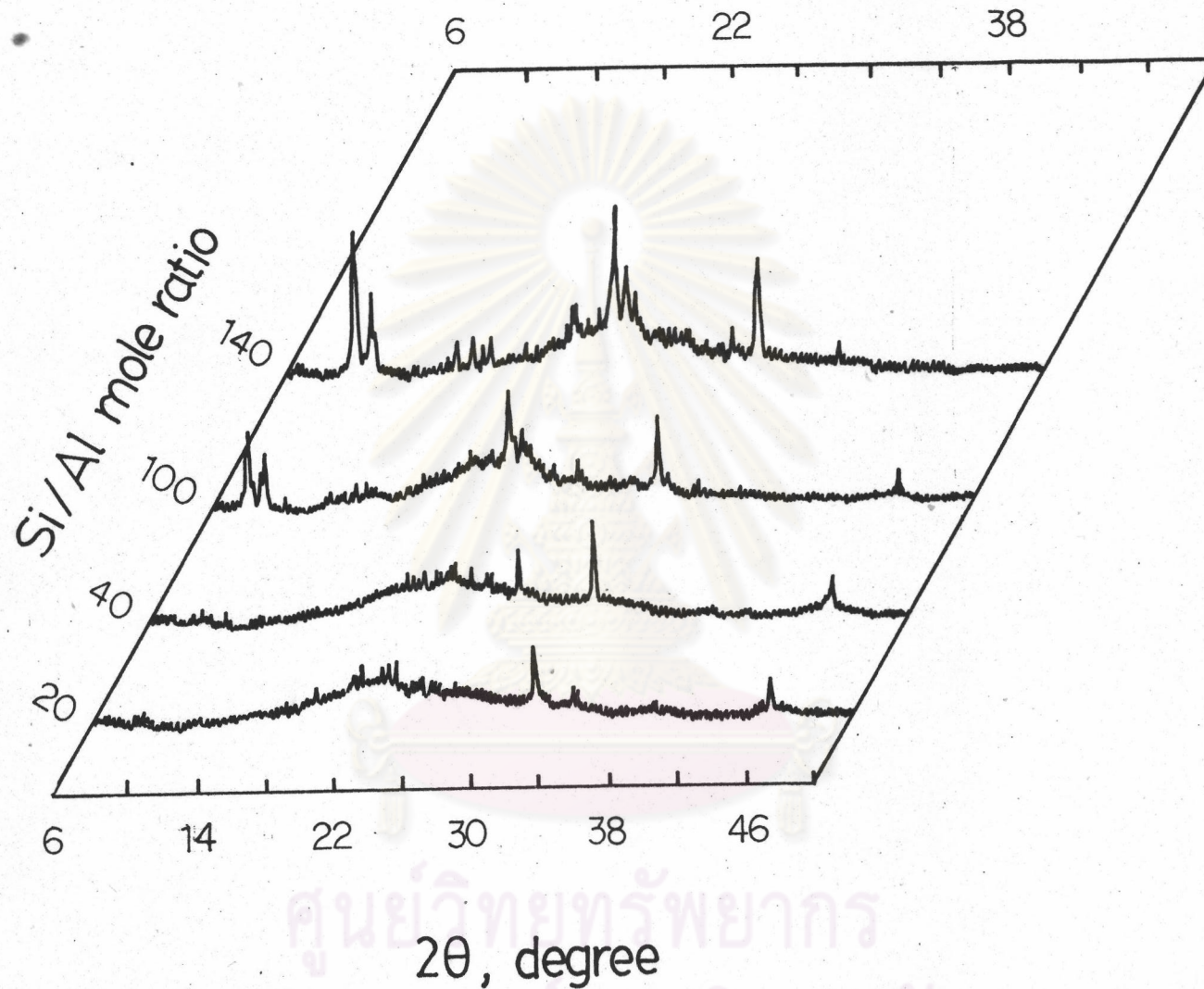


Figure 4.2.2 XRD patterns of pentasil zeolites from various Si/Al mole ratios at initial pressure 5 kg/cm² (gauge)

type of crystal. However, it was suggested that the crystal of very few developed peak was zeolite because of its position on XRD-pattern. In this product crystals there were NaCl crystals mixed with the others. The NaCl peak of XRD-pattern was high intensity even if the crystal was small, however, it had not the effect on XRD-pattern except the appearance of NaCl peak at 32° .

At Si/Al mole ratio 40, peak intensity was higher than that at Si/Al mole ratio 20 but it would rather had low crystallinity. However, it could be specified that this crystal was zeolite by using the above mentioned method. There was NaCl crystal contaminated with other product crystal which was detected on the XRD-pattern.

At Si/Al mole ratio 100, the product crystal had amorphous forms. The crystallinity was not found. From XRD-pattern, this case could not indicate the type of the crystal, because XRD-data was not enough to interpret the results.

At Si/Al mole ratio 140, the crystal peak was well-developed and gave the clear pattern of pentasil zeolite. After calculation for d-values and examination of the data from powder diffraction file, it was found that this crystal was ZSM-5 zeolite. Its crystallinity was medium and the NaCl peak was not found in XRD-pattern. When the crystallinity of all product crystals was compared with each other, the crystallinity of ZSM-5 zeolites was mostly increased with the increasing of Si/Al mole ratio in the range of 20 and 140 and was the highest at Si/Al mole ratio 140. Therefore, at this initial pressure, the optimum Si/Al mole ratio for ZSM-5 synthesis also was 140 among the mentioned range.

From fig. 4.2.2, the XRD-patterns of each Si/Al mole ratio at initial pressure 5 kg/cm^2 (gauge) were nearly the same as XRD-patterns at initial pressure, 1 kg/cm^2 (gauge) except at Si/Al mole

ratio 100, XRD-peak of ZSM-5 zeolite appeared. When the crystallinity of all product crystals were compared with the others, illustrated that the crystallinity of ZSM-5 zeolites were increased with increasing of Si/Al mole ratio in the range of 20 and 140. So was the initial pressure of 1 kg/cm² (gauge), the highest crystallinity of XRD-patterns was at Si/Al mole ratio 140 which was the optimum value for mole ratio of Si/Al.

When the XRD-pattern of pentasil zeolites were compared at different initial pressure by selecting the optimum Si/Al mole ratio at 140, the results were shown in fig 4.2.3. At this mole ratio, the crystallinity of product crystals were highest and clearest when compared with other mole ratios of Si/Al at the same initial pressures. Therefore, it was concluded that, this mole ratio was the best value for crystal synthesis in the range of Si/Al mole ratio 20 and 140. In fig. 4.2.3 all XRD-patterns showed clearly that there was ZSM-5 zeolite. Comparing XRD-patterns to each other for the conclusion of the optimum initial pressure used in crystallization period, this figure illustrated that the initial pressure of 3 kg/cm² (gauge) was the optimum pressure and the order of initial pressure for ZSM-5 crystallization product was 3 > 5 > 1, so that the optimum pressure which could be used in crystal synthesis in the range of initial pressure 1 and 5 kg/cm² (gauge) and Si/Al mole ratio 20 and 140 was at the pressure of 3 kg/cm² (gauge).

From the above conclusion, the Si/Al mole ratio and initial pressure in the crystallizer which were now the best conditions were 140 and 3 kg/cm² (gauge), respectively. The crystallinity of product crystal were plotted versus various Si/Al mole ratios and was shown in fig. 4.2.4. The results from this figure were the same as those discussed before. The crystallinity of product crystals was all increased with the increasing of Si/Al mole ratio in the range of 20 and 140 and at

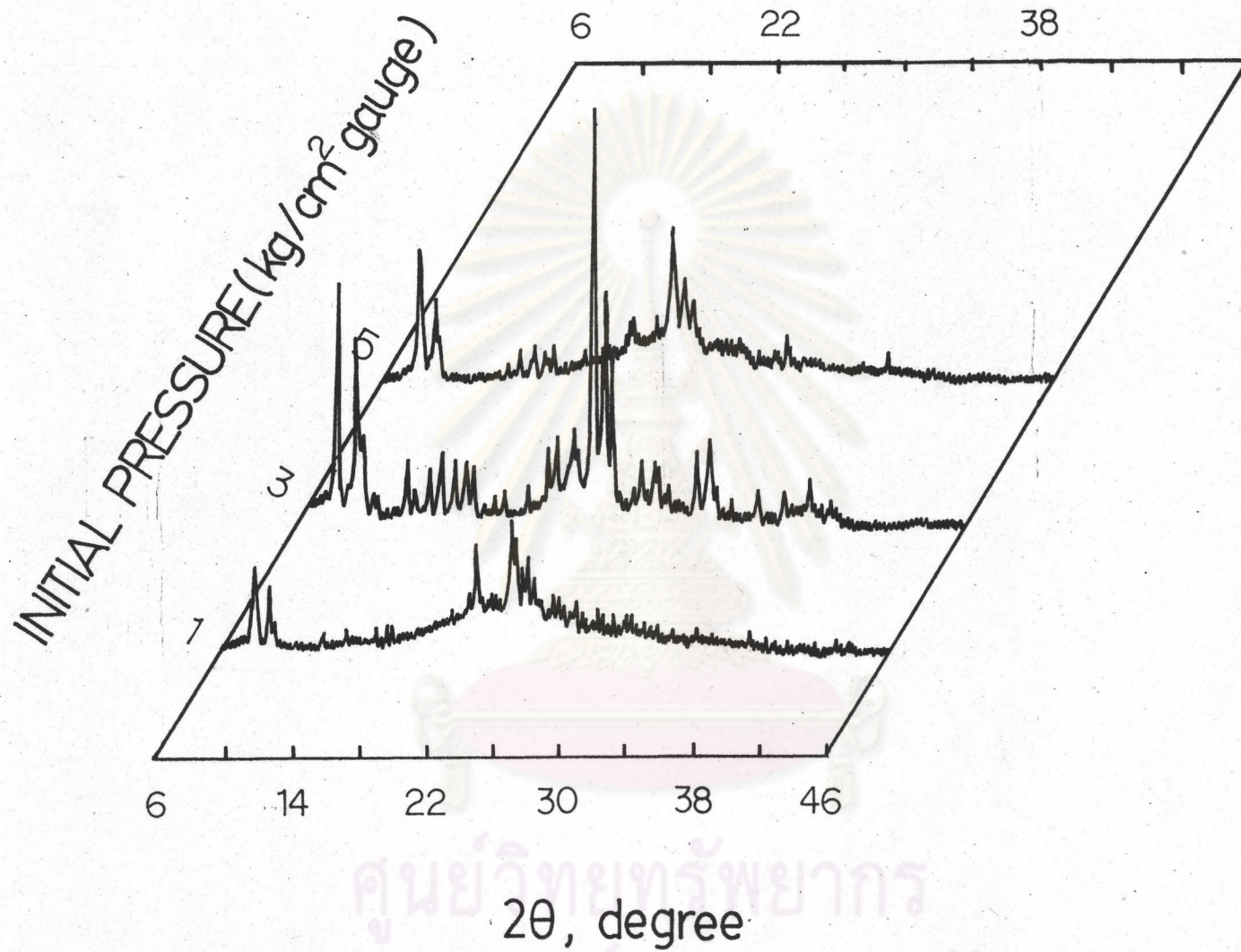


Figure 4.2.3 XRD patterns of pentasil zeolites at various initial pressure (Si/Al mole ratio 140)

Si/Al mole ratio 140, the crystallinity of all product crystals at various initial pressure were at it maximum. Various initial pressure affected the crystallinity of crystal product, for initial pressure 1 and 5 kg/cm²(gauge), the crystallinity of each Si/Al mole ratio were low and initial pressure 3 kg/cm² (gauge) was higher than the others. Therefore, at Si/Al mole ratio 140 and initial pressure 3 kg/cm² (gauge) in the crystallizer were the best conditions for crystal synthesis in these mentioned range.

4.2.2 External structure analysis by scanning electron microscope.

In the study of effect of initial pressure on product crystals by SEM, Si/Al mole ratio 140 was chosen because of the highest crystallinity of product crystals when compared with other ones. SEM photomicrographs of these product crystals were shown in figs. 4.2.5, 4.1.6, and 4.2.6.

From SEM-photomicrograph of product crystals at initial 1 kg/cm² (gauge) as shown in fig. 4.2.5, all of the products were amorphous and had small size which were solidly constructed. There was no ZSM-5 crystal developed in this synthesis, so that, from these results, it was suggested that ZSM-5 crystal were more slowly developed than the other at initial pressure 5 kg/cm² (gauge) (fig. 4.2.6), ZSM-5 developed about 80-85% of product crystals. The ZSM-5 product crystals had whole sizes at 10 μ m. So this pressure was the optimum condition for ZSM-5 synthesis. The result of product crystals at initial pressure 3 kg/cm² (gauge) was as same as the one at 5 kg/cm² (gauge) excepted the higher percentage of ZSM-5 crystal (about 90%). It was concluded that the most optimum condition for initial pressure which was used in ZSM-5 synthesis was 3 kg/cm² (gauge).

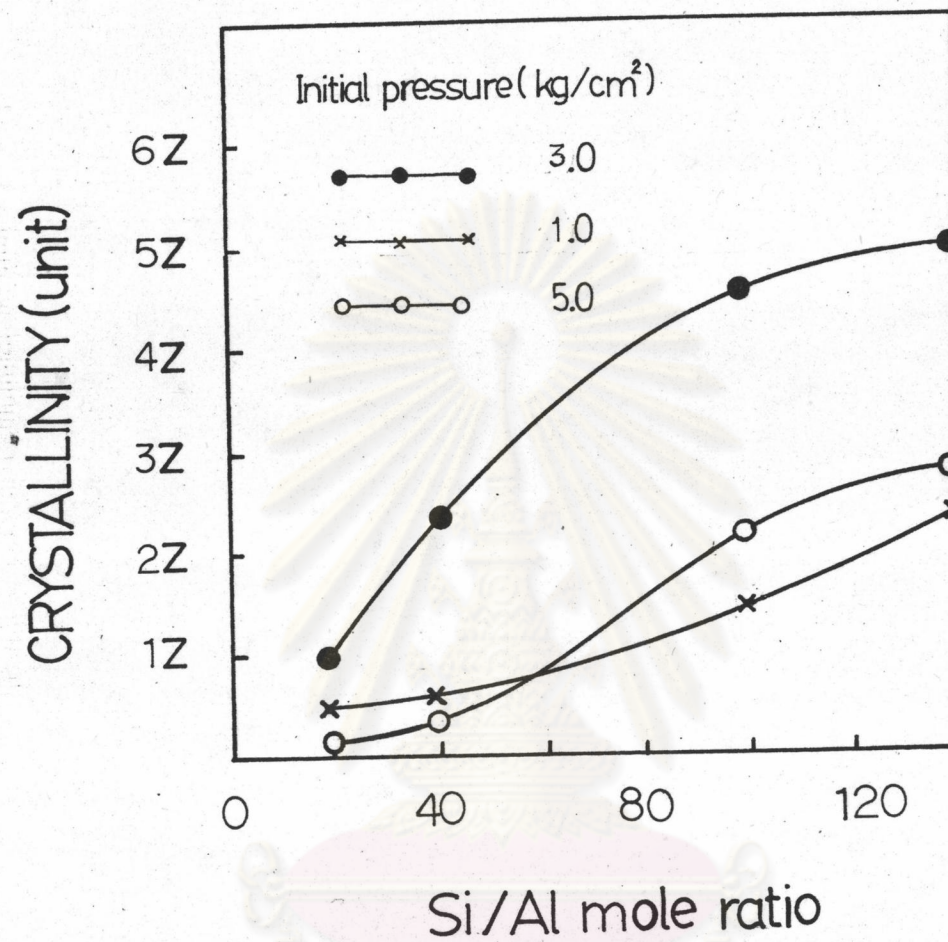


Figure 4.2.4 Crystallinity of product crystals at various Si/Al mole ratio

4.2.3 Functional groups analysis

Infrared spectra of zeolites at various initial pressures were shown in fig.4.2.7., at initial pressure 3 kg/cm²(gauge), there were strong bands of asymmetric stretching (950-1,250 cm⁻¹) and T-O bending (420-500 cm⁻¹) of internal tetrahedra and double ring (500-650 cm⁻¹) and symmetric stretching (750-820 cm⁻¹) of external linkages. In the case of initial pressure 1 and 5 kg/cm² (gauge), the bands of symmetric stretching and double ring of external linkages were weaker than at initial pressure 3 kg/cm²(gauge), therefore initial pressure 3 kg/cm²(gauge) was the most optimum condition in ZSM-5 synthesis.

4.2.4 Chemical element analysis

From No.4.2.4, in table 4.1, real Si/Al mole ratio was the highest at initial pressure 3 kg/cm²(gauge) so that at this pressure, the amounts of silicon in product crystal was the highest (when compared with the other pressures and based on the same amounts of aluminum).

There were illustrated that the results from different methods of product crystals analysis which mentioned above were all same so it was concluded that initial pressure 3 kg/cm²(gauge) was the best condition in ZSM-5 zeolites synthesis.

4.3 pH of mixing solution

The study of pH effects on crystal structure were used Si/Al mole ratio in wide range (Si/Al mole ratio 2-400) and the results were interesting.

4.3.1 Characterization of product crystals by crystallinity analysis.

At Si/Al mole ratio 2, XRD-patterns for pentasil zeolite from various pH of mixing solution were shown in fig. 4.3.1. At pH 6, XRD-pattern showed that the product crystals were Sodium silicate

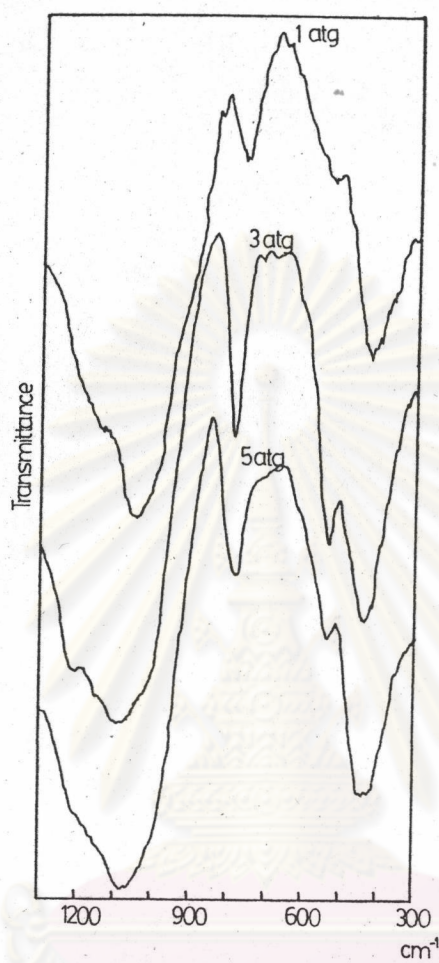


Figure 4.2.7 IR spectra of product crystals at various initial pressure

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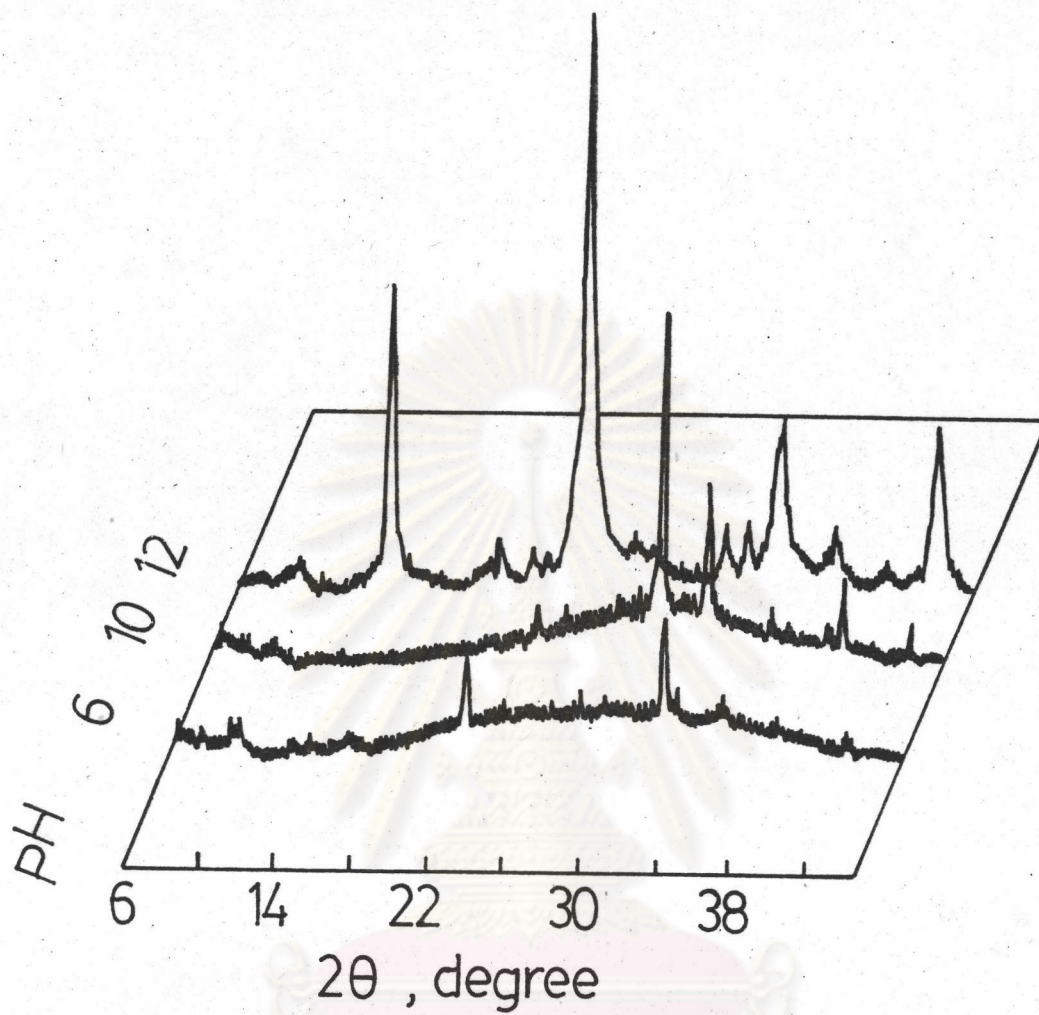


Figure 4.3.1 XRD patterns for pentasil zeolites from various pH of mixing solution at Si/Al mole ratio 2

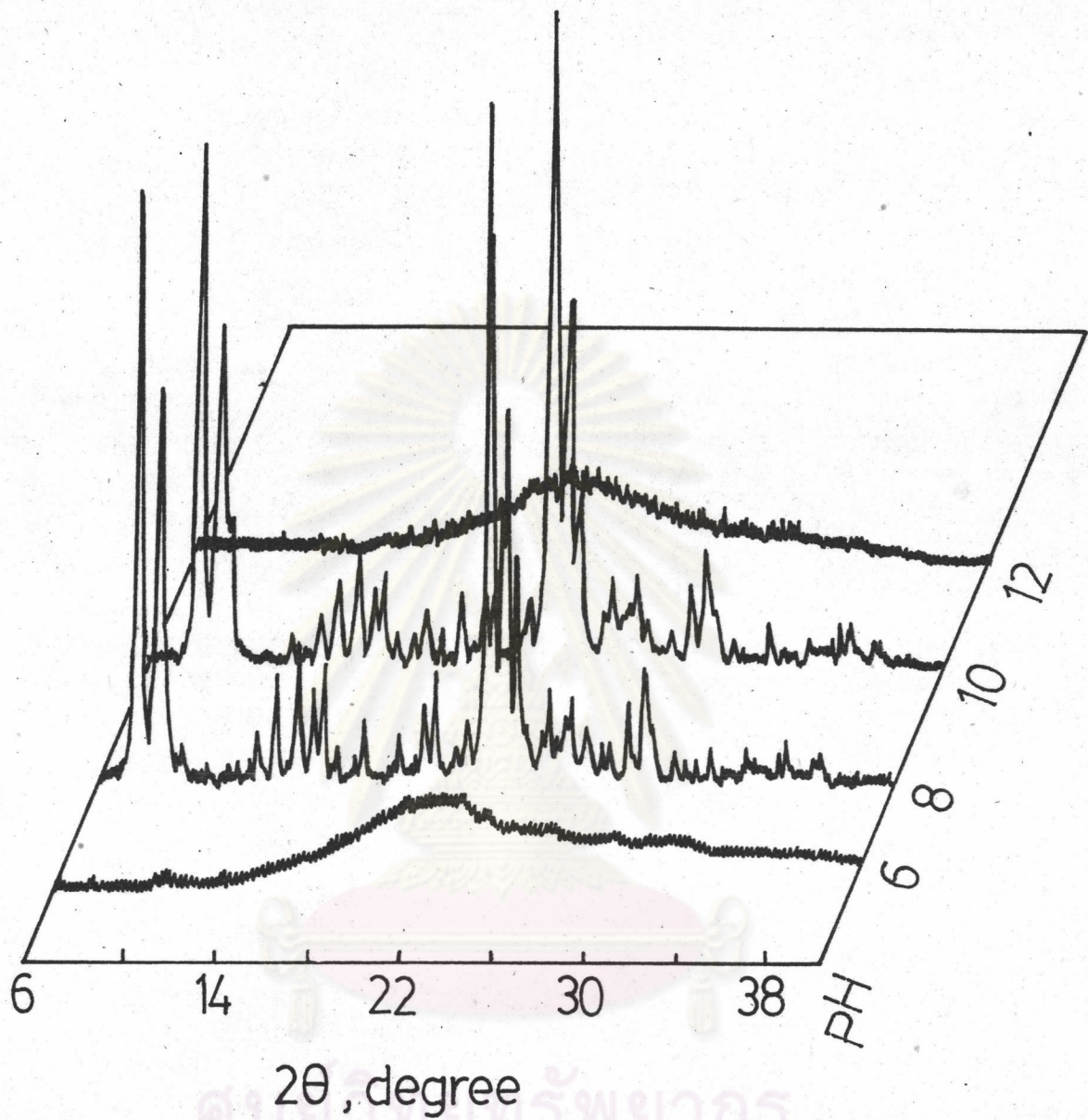


Figure 4.3.2 XRD patterns for pentasil zeolites from various pH of mixing solution at Si/Al mole ratio 100

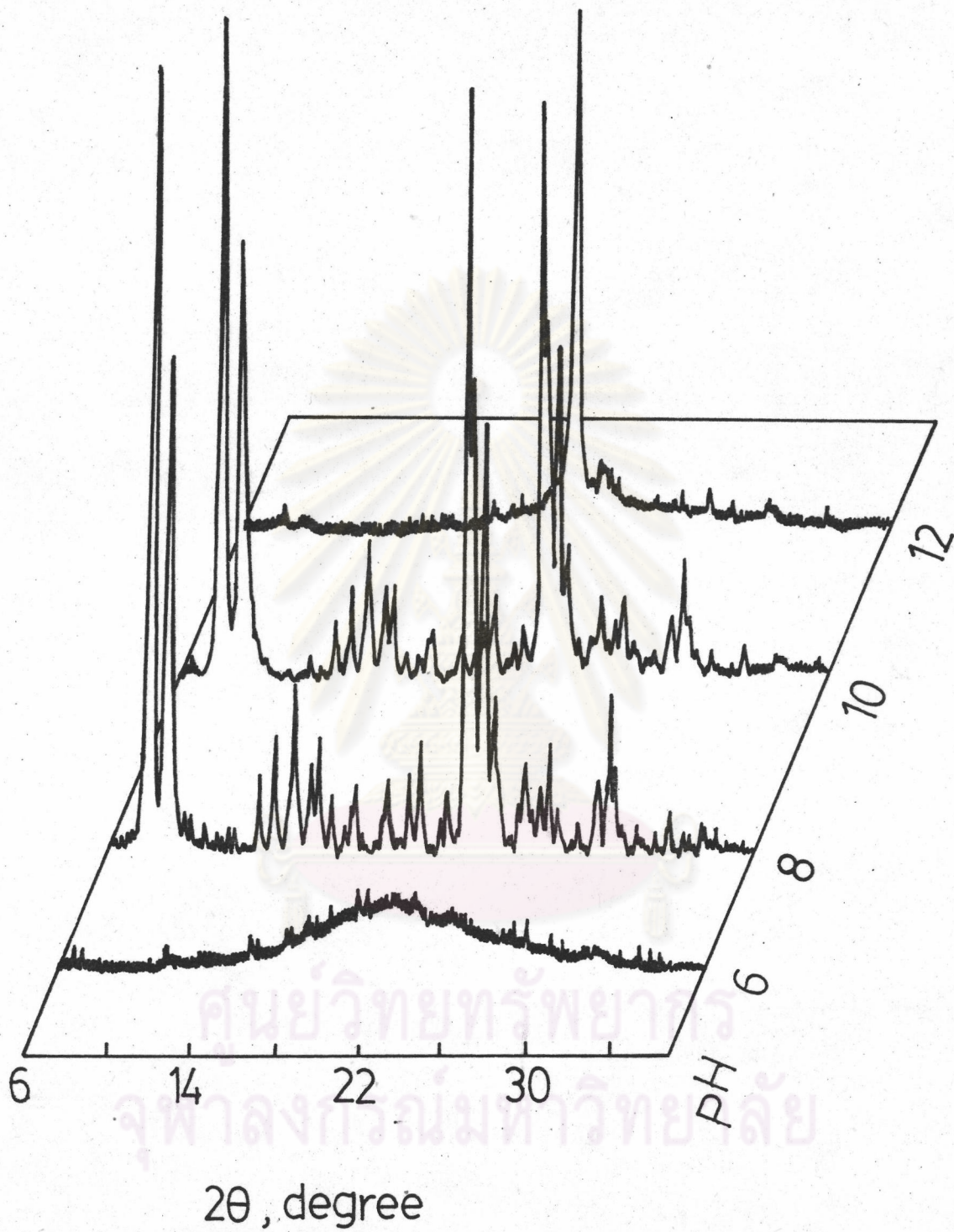


Figure 4.3.3 XRD patterns for pentasil zeolites from various pH of mixing solution at Si/Al mole ratio 200

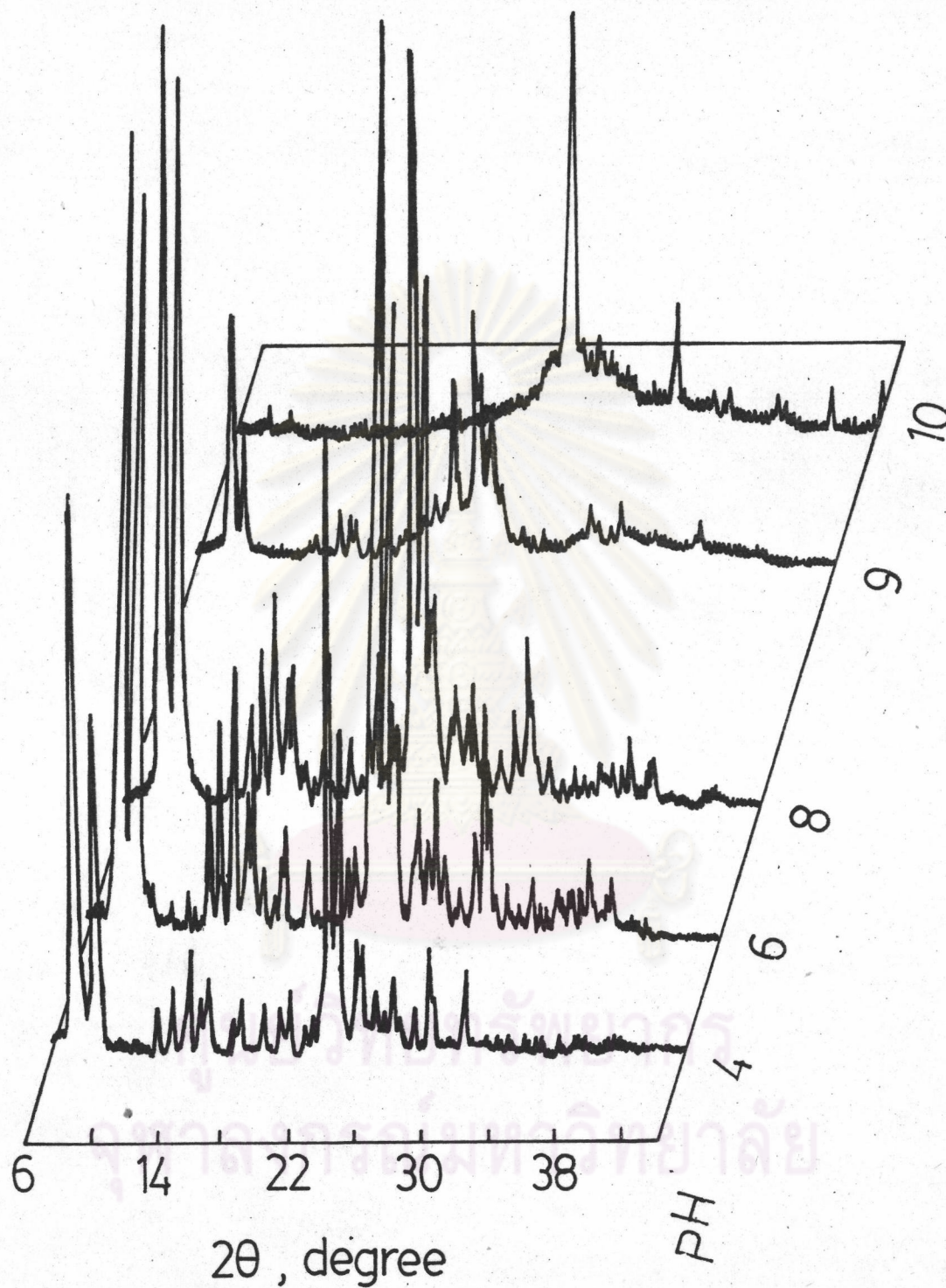


Figure 4.3.4 XRD patterns for pentasil zeolites from various pH of mixing solution at Si/Al mole ratio 400

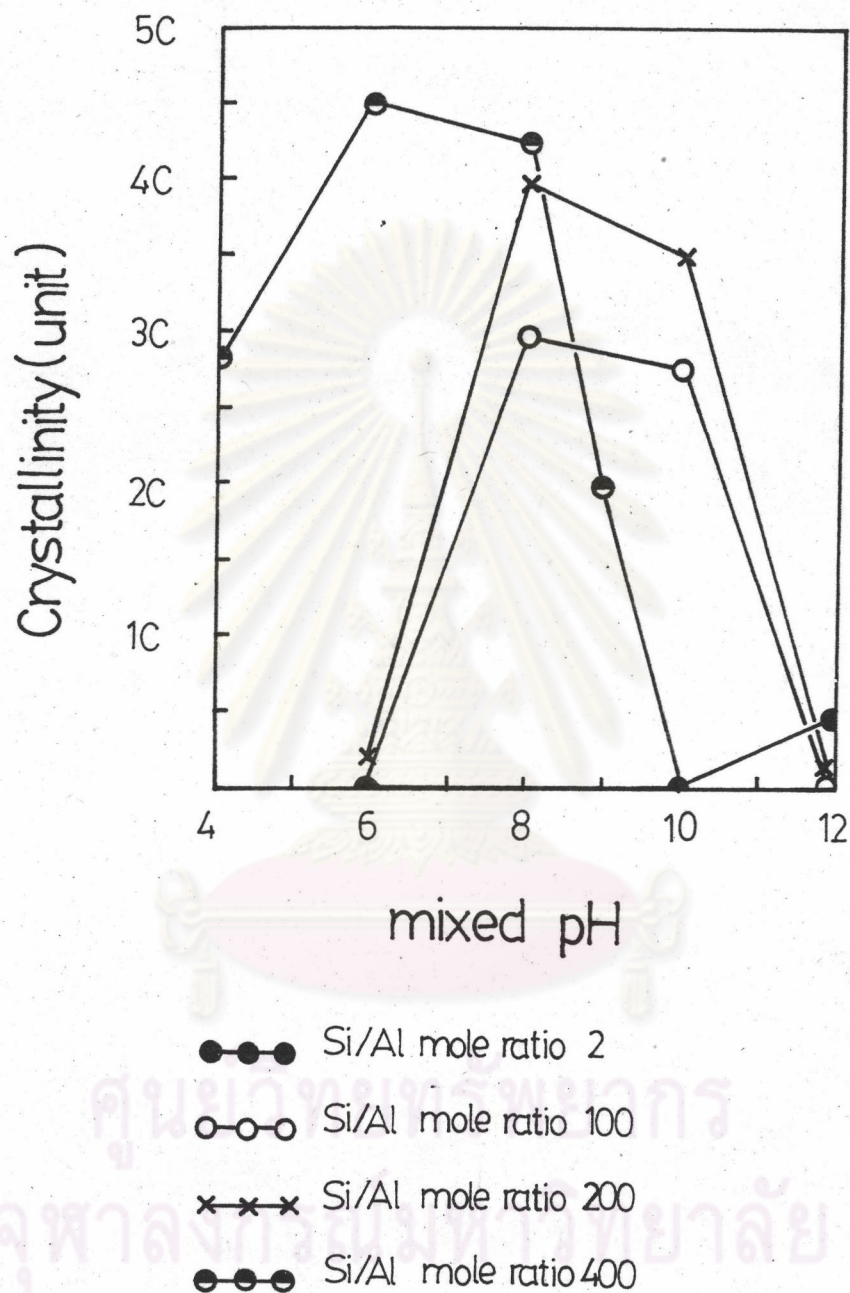


Figure 4.3.5 Crystallinity of product crystals at various Si/Al mole ratio and pH

hydrate ($\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$). Therefore, this pH was not suitable condition in pentasil zeolite synthesis and alumina could not form bond with silica to get aluminosilicate compounds, so that the crystallinity of zeolite was zero.

At mixed pH 10 of this Si/Al mole ratio, XRD-pattern showed that this conditions was not optimum for ZSM-5 zeolite synthesis too, because the product crystals were zeolite (aluminosilicate structure) which were not ZSM-5.

For mixed pH 12, the result of XRD-pattern showed that product crystals were sodium aluminium silicate hydrate ($\text{Na-Al-SiO}_3 \cdot \text{H}_2\text{O}$). These were not ZSM-5 zeolite, so were those ones at pH 10.

When all of results were compared with each other, they were shown that when mixed pH was increased, alumina could increased in the bond forming with silica obtain get aluminosilicate frameworks. But all of product crystals were not ZSM-5, so at Si/Al mole ratio 2 in mixed pH range 6-12, were not suitable condition to synthesis ZSM-5 zeolite.

At Si/Al mole ratio 100, XRD-patterns were shown in fig. 4.3.2. From this figure, it was no peaks in the product crystals of mixed pH 6, hence, this condition was not suitable for ZSM-5 synthesis. At mixed pH 8, XRD-pattern showed the clearly peaks of ZSM-5 crystals, the crystallinity was very high, so was at mixed pH 10 and crystallinity of mixed pH 10 was much higher than that one at pH 8. But in the case of mixed pH 12, XRD-patterns was the same as at pH 6, in consequence, the most optimum pH for ZSM-5 synthesis at Si/Al mole ratio 100 was pH 10.

At Si/Al mole ratio 200, XRD-patterns for product crystal from various pH of mixing solution were shown in fig. 4.3.3. Almost of results were as same as at Si/Al mole ratio 100 but the crystallinity of

ZSM-5 product crystal at mixed pH 8 was much higher than that one at pH 10. It was concluded that at Si/Al mole ratio 200, the most optimum pH for ZSM-5 synthesis was pH 8.

At Si/Al mole ratio 400, XRD-pattern of product crystals were shown in fig. 4.3.4. For pH of mixing solution 4, the result from XRD-pattern illustrated that all of product crystals were ZSM-5. For this reason, acidic pH was shown to have the effectiveness on ZSM-5 zeolite synthesis. At mixed pH 6, 8, and 9, the results were the same as that one at pH 4 and for mixed pH 10, XRD-pattern showed that the product were the other type of zeolite which could not specify type certainly. There was the observation that, at mixed pH 12 in preparation step of catalyst, crude catalyst was not appear. When the results were compared together, the order of ZSM-5 crystallinity for ZSM-5 preparation were as follows : mixed pH 6 > 8 > 4 > 9.

All results from various Si/Al mole ratio and pH of mixing solution were compiled together, as shown in figs. 4.3.5. there were illustrated the crystallinity of product crystals at various Si/Al mole ratio and mixed pH that at Si/Al mole ratio 2, ZSM-5 zeolite could not developed, when Si/Al mole ratio increased, high percentage of ZSM-5 crystals were developed and maximum crystallinity of ZSM-5 crystals were varied related with both Si/Al mole ratio and mixed pH. Mixed pH which gave the maximum crystallinity of ZSM-5 at Si/Al mole ratio 100, 200, and 400 were pH 10, 8 and 6, respectively.

4.3.2 External structure analysis by scanning electron-microscope.

SEM-photomicrographs of product crystals from the study of effect of mixed pH at various Si/Al mole ratio were shown in fig. 4.3.6 - 4.3.21.

At Si/Al mole ratio 2, for mixed pH 8, SEM-photomicrograph (fig. 4.3.6 showed amorphous forms of product crystals. The products composed with many phases, other phases were spherical type, small granules and the other were non-geometric forms with large size. Therefore, this pH could not use to prepare ZSM-5 catalyst. For mixed pH 12, SEM-photographs were shown in figs. 4.3.8 and 4.3.9, the product crystals were spherical form with size of 0.3-1.0 μm . On each crystal, it was ununiformly composed of many microtubules until it had spherical-formed granules. For this reason, it was suggested to be the first forms which would developed to be ZSM-5 crystal, finally.

For the study of effects of mixed pH at Si/Al mole ratio 100, at pH 8, SEM-photograph was shown in fig. 4.3.7, the products contained with 95% of ZSM-5 crystals approximately and there were little impurities contaminated with ZSM-5 crystals. The crystals had spherical form with the same size at about 8 μm . It was illustrated that, this mixed pH was one of the optimum conditions which was used to synthesis ZSM-5 catalyst. The result of SEM-photograph of product crystals at mixed pH 10 was almost the same as at pH 8 (fig. 4.3.10), all of the product crystals were spherical formed with same size about 6-7 μm . of ZSM-5 crystals. There was no impurity in product crystals. For mixed pH 12, the SEM photograph was shown in fig.4.3.11, crystal was amorphous with many forms which were non-geometry, consequently, this pH was not the optimum condition for ZSM-5 synthesis. When all results of each mixed pH at Si/Al mole ratio 100 were compared with the others, the conclusion for optimum conditions in preparing of ZSM-5 were ordered as follows: pH 10 > 8.

For the study of zeolite synthesis at Si/Al mole ratio 200, SEM-photographs of product crystals of various mixed pH were shown in figs. 4.3.12 - 4.3.14. At mixed pH 8 (fig. 4.3.12), SEM-photograph showed that the product crystals were cubic-spherical form contained

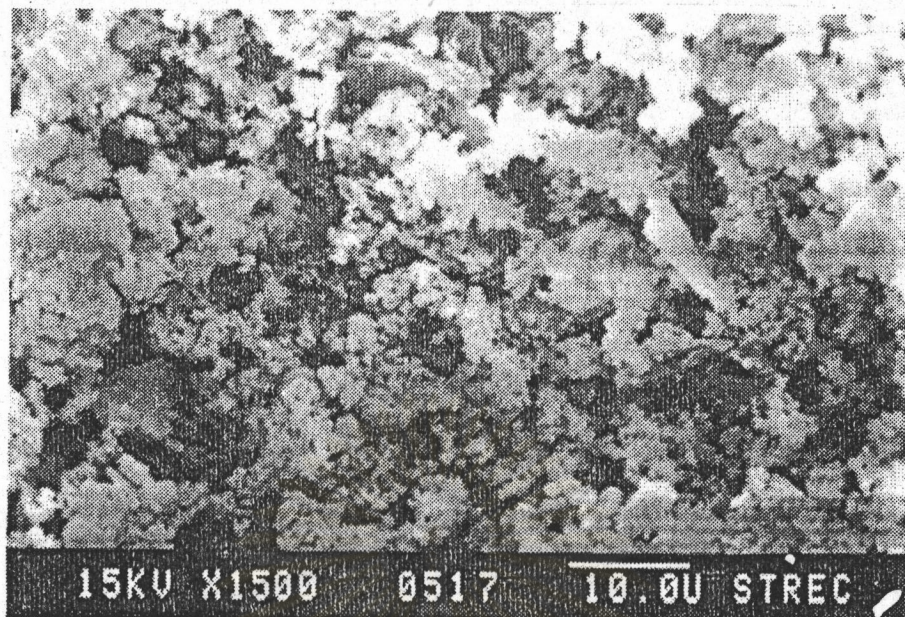


Figure 4.3.6 SEM photograph of product crystals at Si/Al mole ratio 2 and pH8

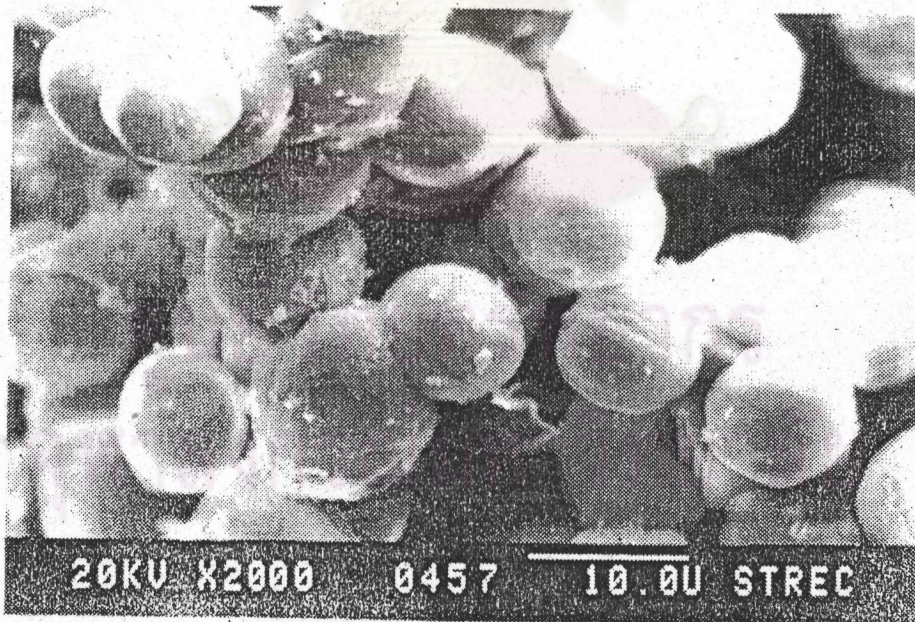


Figure 4.3.7 SEM photograph of product crystals at Si/Al mole ratio 100 and pH8



Figure 4.3.8 SEM photograph of product crystals at Si/Al mole ratio 2 and pH 12



Figure 4.3.9 SEM photograph of product crystals at Si/Al mole ratio 2 and pH 12

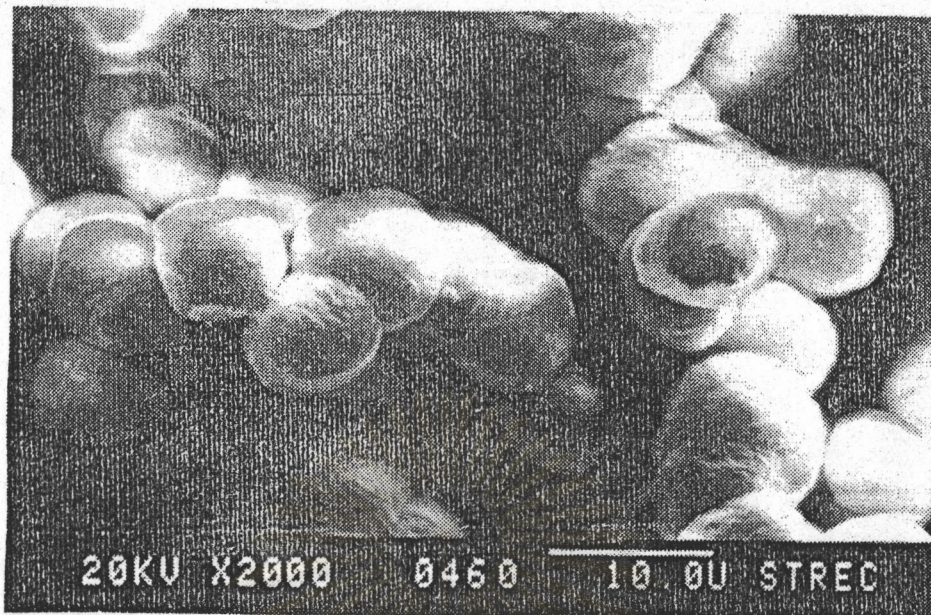


Figure 4.3.10 SEM photograph of product crystals at Si/Al mole ratio 100 and pH 10

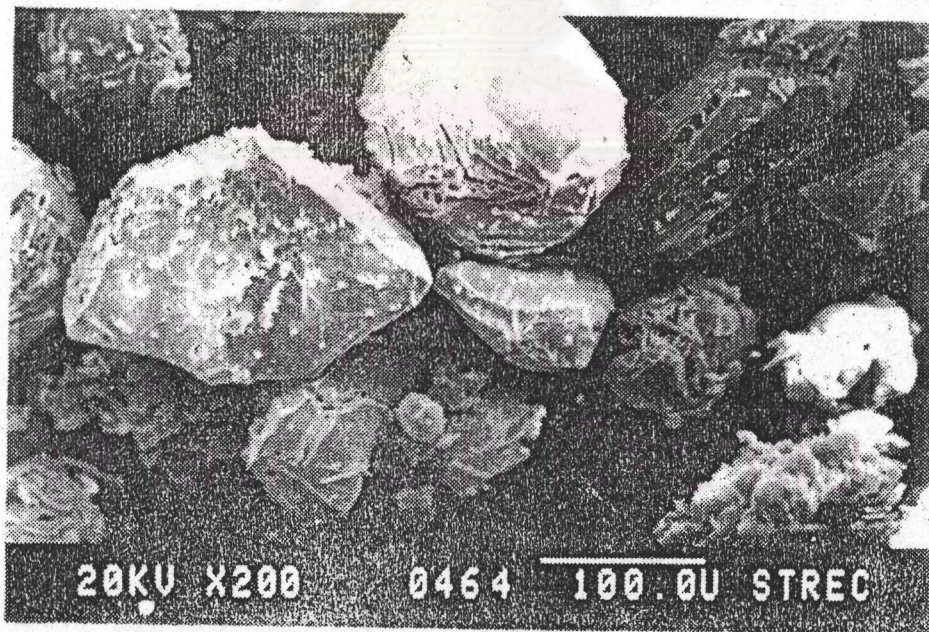


Figure 4.3.11 SEM photograph of product crystals at Si/Al mole ratio 100 and pH 12

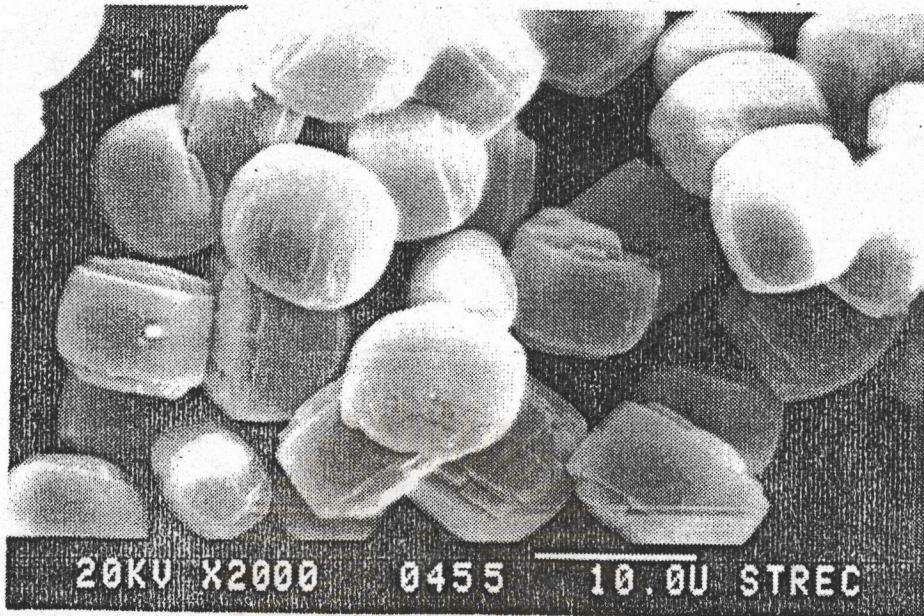


Figure 4.3.12 SEM photograph of product crystals at Si/Al mole ratio 200 and pH 8

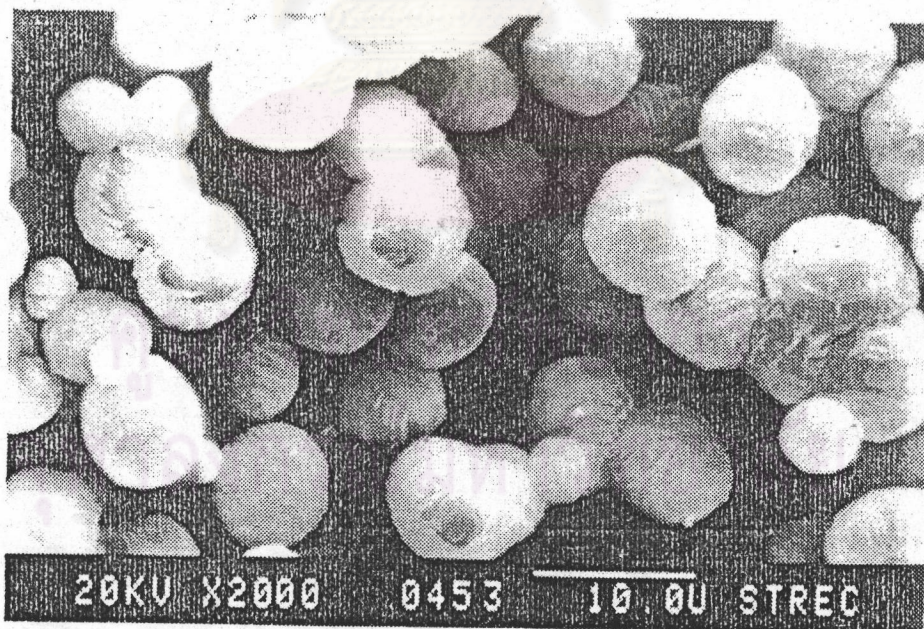


Figure 4.3.13 SEM photograph of product crystals at Si/Al mole ratio 200 and pH 10

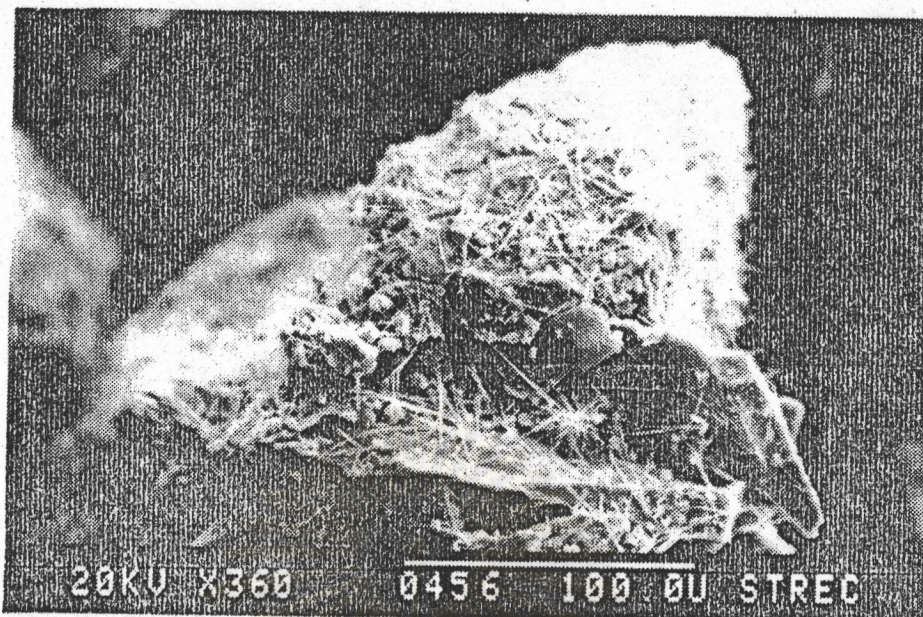


Figure 4.3.14 SEM photograph of product crystals at Si/Al mole ratio 200 and pH 12

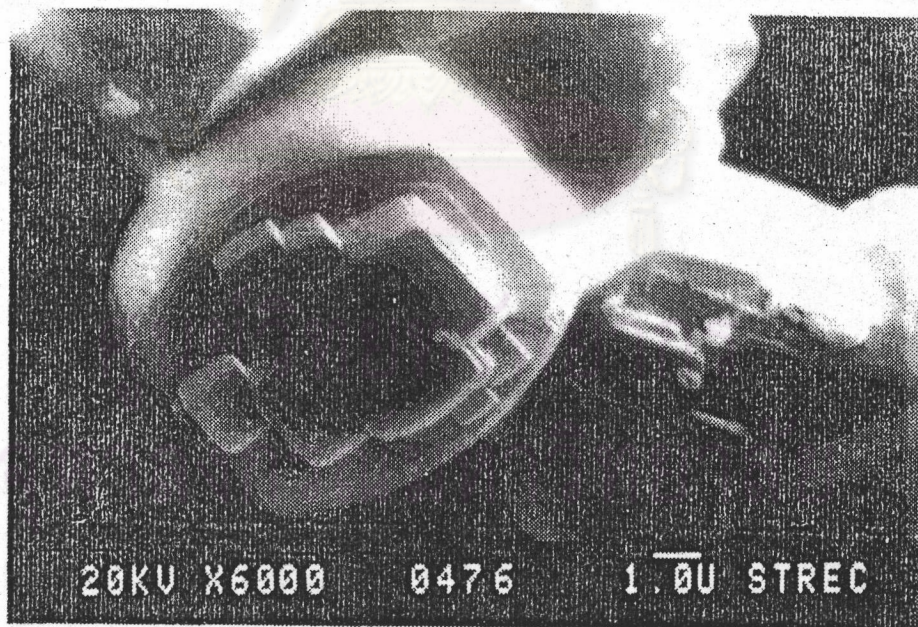


Figure 4.3.15 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 4

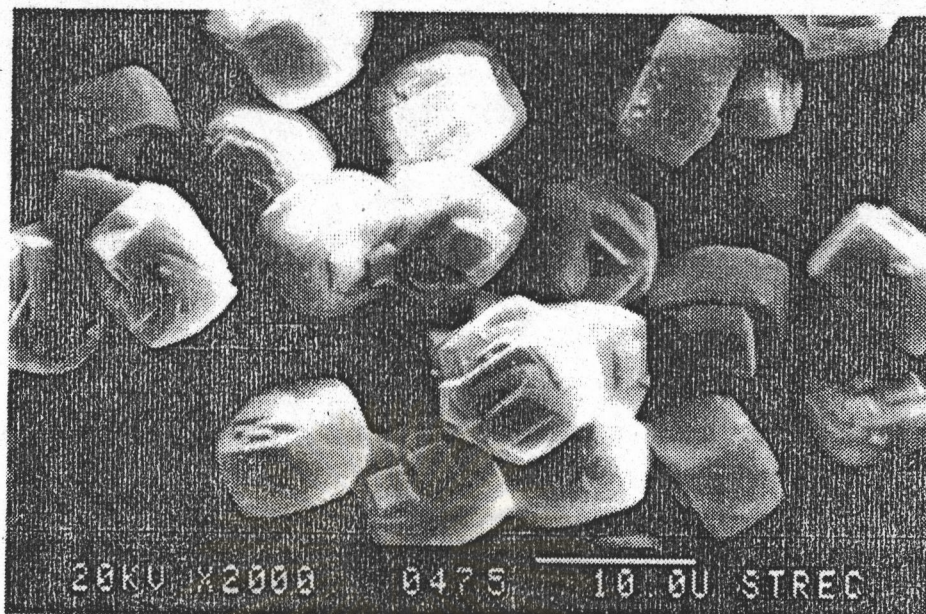


Figure 4.3.16 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 4

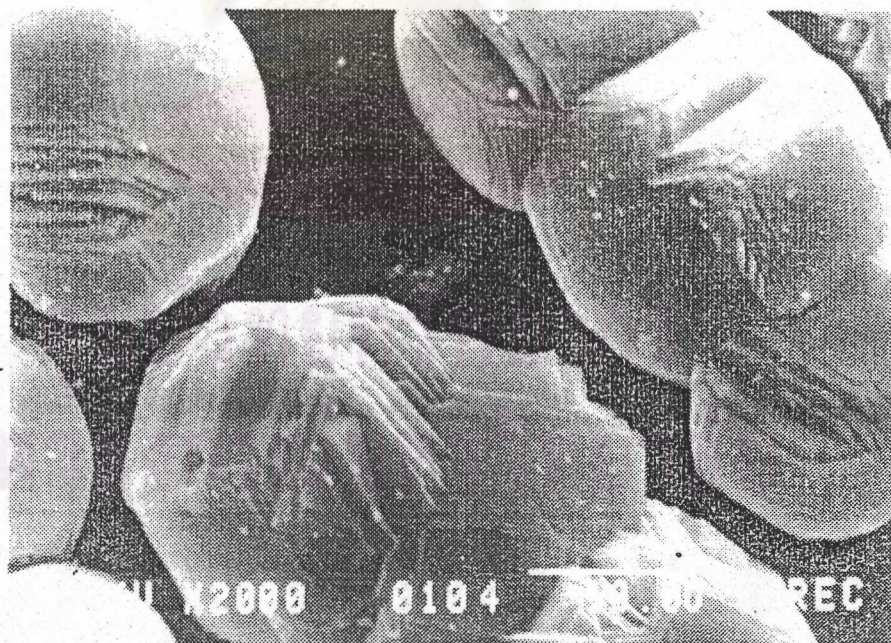


Figure 4.3.17 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 6

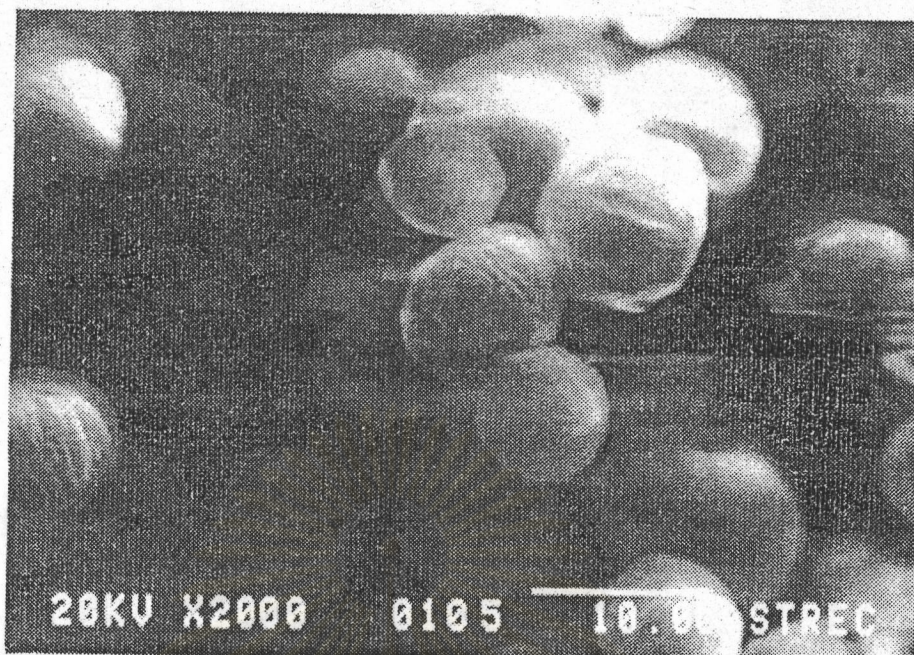


Figure 4.3. 18 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 8

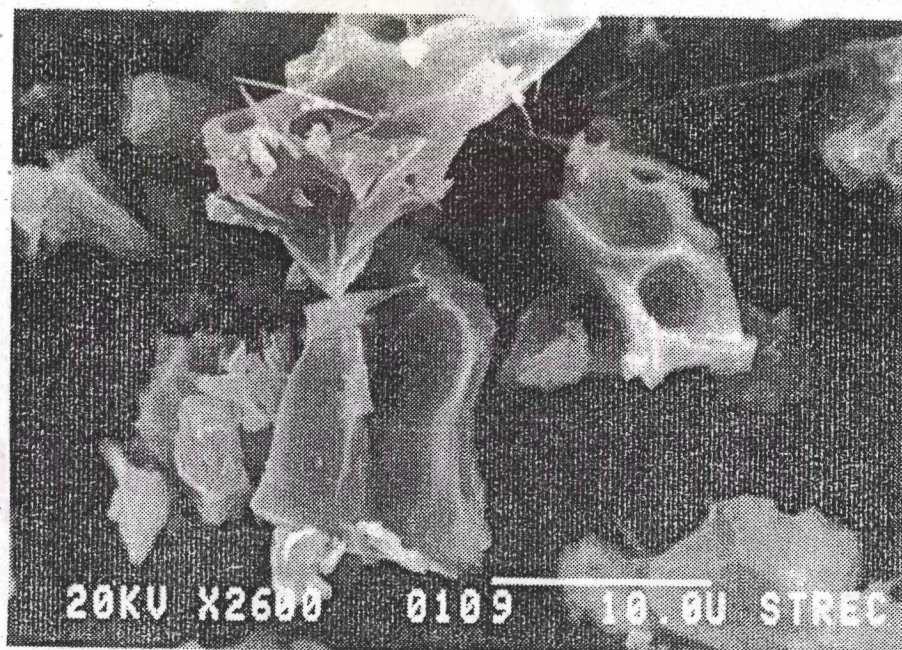


Figure 4.3. 19 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 10

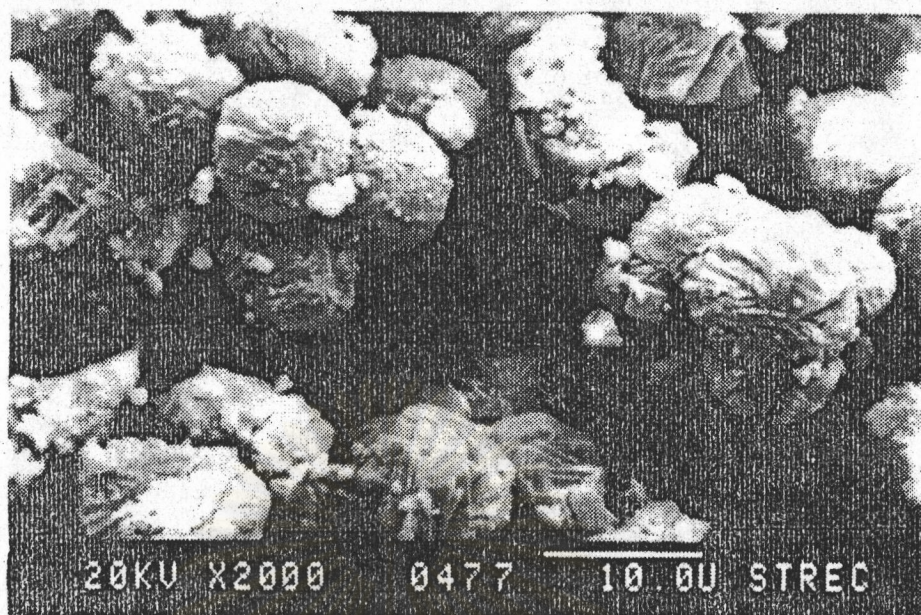


Figure 4.3. 20 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 9

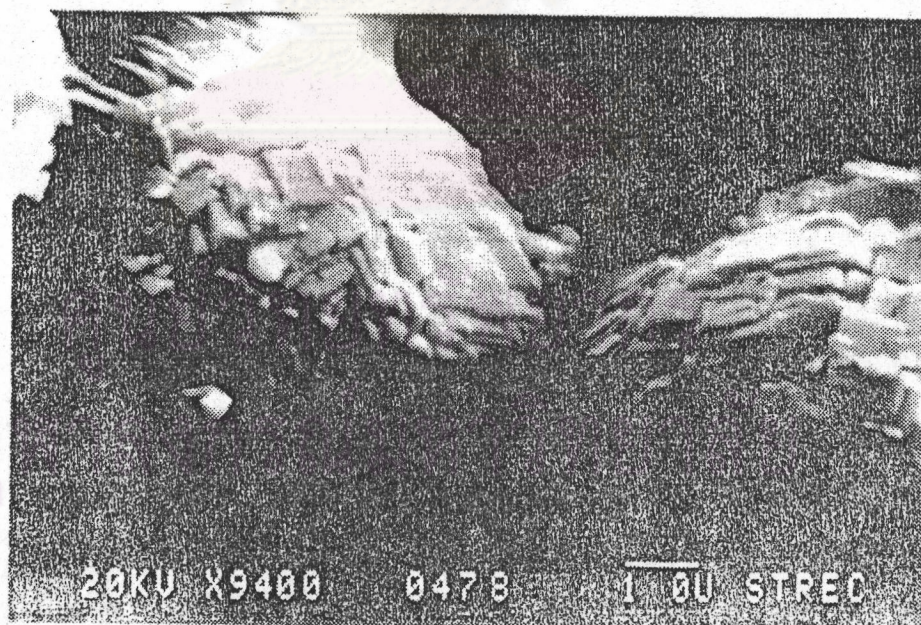


Figure 4.3.21 SEM photograph of product crystals at Si/Al mole ratio 400 and pH 9

with some sphere form. The mean size was about 8 μm . These two forms of crystals were ZSM-5 zeolite. There was observed that cubic-spherical form of crystal could developed to be spherical form finally, by adding crystal sheets. Therefore this pH was optimum for ZSM-5 synthesis. In fig. 4.3.13 (mixed pH 10), the crystals were spherical forms with 6 μm size. There were very few impurities contained with ZSM-5 product crystals, so was pH 8, this pH was optimum to use in ZSM-5 synthesis. But at mixed pH 12, result from SEM-photograph in fig. 4.3.14 illustrated that product crystals composed with amorphous granular form, needle-formed crystal, large-sized amorphous product, and many impurities, so that, this pH was not a good condition to prepared ZSM-5 zeolite. Wherefore, the optimum pH for ZSM-5 synthesis at Si/Al mole ratio 200 were pH 8 and pH 10, respectively.

At Si/Al mole ratio 400, the results were very interesting, as shown in figs. 4.3.15 and 4.3.16 of SEM-photographs of product crystals for mixed pH 4. These two figures had different multiplicity. Figure 4.3.15 had the multiplicity at 6,000 and fig. 4.3.16 had the multiplicity at 2,000. All product crystals were going to be cubic-spherical form by development of crystal sheets. They had the same size about 8 μm . Figure 4.3.15 showed clearly that the development of crystal from small size to large size started from the center of the sheet on crystal and spreaded until covered the former sheet, afterward, the crystal would developed now sheet subsequently. Wherefore, acidic pH could used to be mixed pH in zeolite synthesis. For mixed pH 6 and 8, the results from SEM-photographs were same. Almost of the product crystals were ZSM-5 crystals, there were very few of impurities deposited on surface of ZSM-5 crystals. The difference between these two results was the size of crystals. At mixed pH 6, mean size of ZSM-5 crystals was 20 μm but at mixed pH 8, mean size of ZSM-5 crystals was 8

μm . These two product crystals had spherical form. So, mixed pH 6 and 8 were optimum pH in ZSM-5 synthesis. For mixed pH 9, SEM-photographs were shown in figs. 4.3.20 and 4.3.21. There were 70-80% of ZSM-5 crystal in product crystal. At mixed pH 10, SEM-photograph (fig. 4.3.19), showed that the product crystals composed of needed-formed crystal and non-geometric form which were not ZSM-5 zeolite. Therefore, when all results from various were compared with each other, the order of optimum mixed pH was the following: pH 6>8>4>9

As mentioned above, it was suggested that the optimum mixed pH for ZSM-5 synthesis was varied related with Si/Al mole ratio. Wherefore, the most optimum mixed pH was not fixed at constant value, but Si/Al mole ratio was increased, optimum mixed pH was decreased.

4.3.3 Functional groups analysis

Figure 4.3.22 showed IR spectra of product crystal at various pH of mixing solution for Si/Al mole ratio 2. From this figure, at pH 6,8, and 10, there were the appearance of stretching band ($950-1,100\text{ cm}^{-1}$) and Si-OH bending of internal tetrahedra [1] but there was not strong band of T-O bending of internal tetrahedra appeared in this figure. For pH12, there were asymmetric stretching band ($950-1,100\text{ cm}^{-1}$) and T-O bending band ($420-500\text{ cm}^{-1}$) of internal tetrahedra, symmetric stretching band ($700-800\text{ cm}^{-1}$) of external linkages, and double ring band ($600-650\text{ cm}^{-1}$) of external linkages in IR spectra. So at pH 6,8, and 10, the developments of TO_4 tetrahedra frameworks were not complete and at pH 12, product crystals developments were better than the others but these crystals still were not ZSM-5 zeolites, therefore, Si/Al mole ratio 2 was not the suitable condition in ZSM-5 synthesis.

For Si/Al mole ratio 100, IR spectra were shown in fig.4.3.23, product crystals from all pH of mixing solutions showed well-development of primary building unit. The band at $750-820\text{ cm}^{-1}$ was

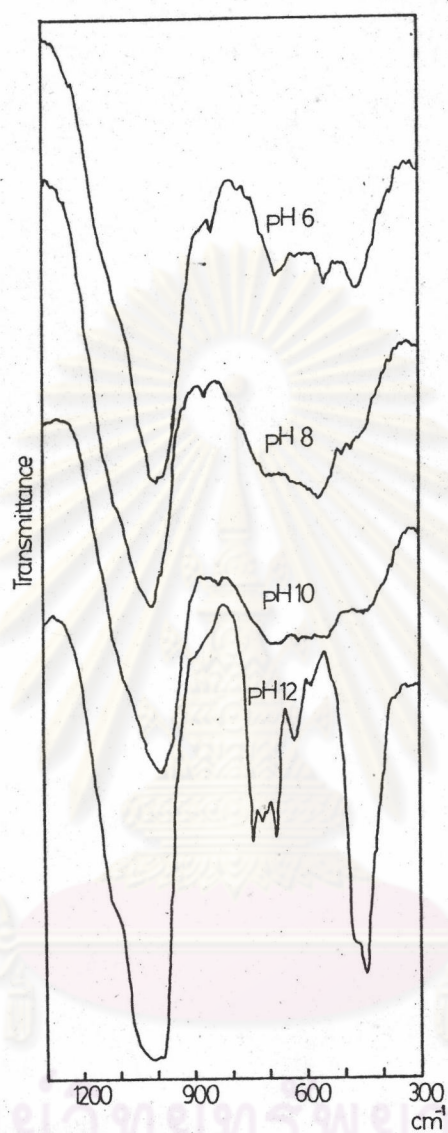


Figure 4.3.22 IR spectra of product crystals for Si/Al mole ratio 2 at various pH

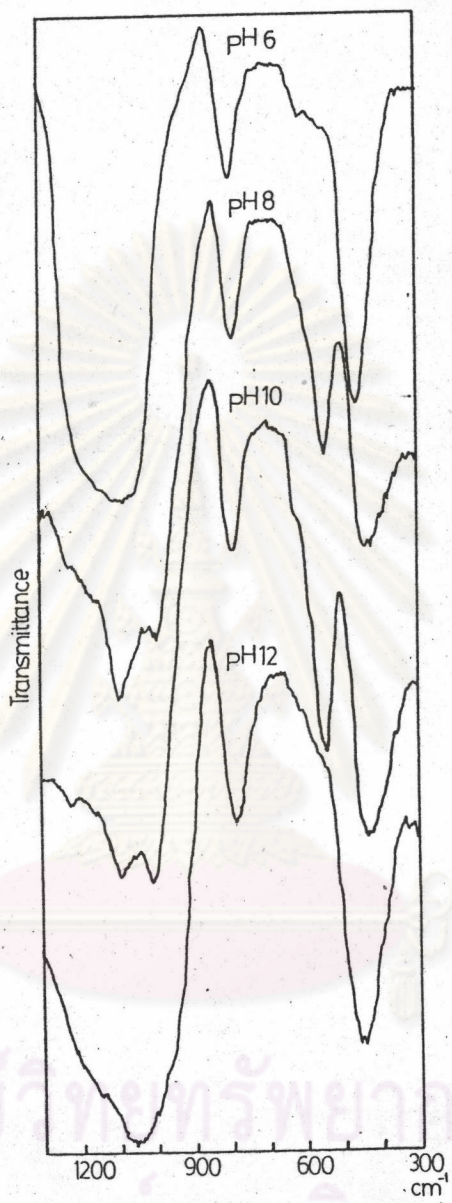


Figure 4.3.23 IR spectra of product crystals for Si/Al mole ratio 100 at various pH

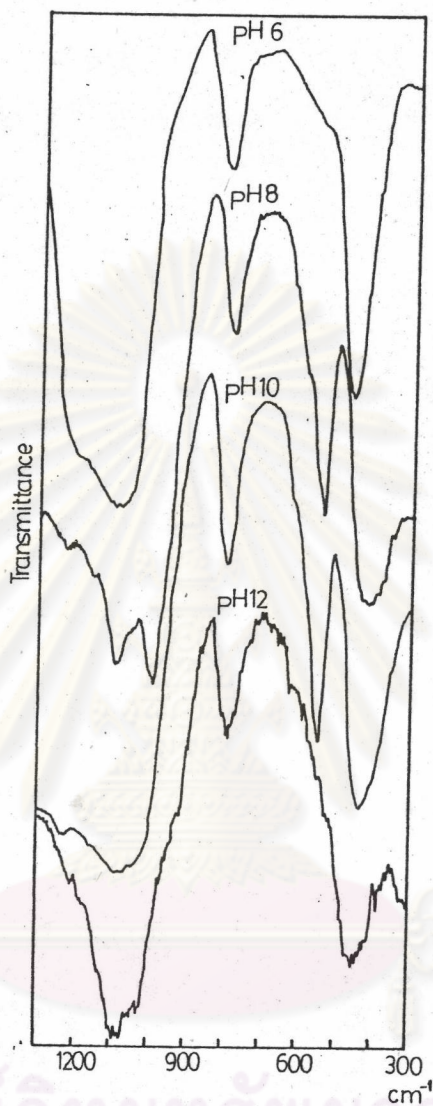


Figure 4.3.24 IR spectra of product crystals for Si/Al mole ratio 200 at various pH

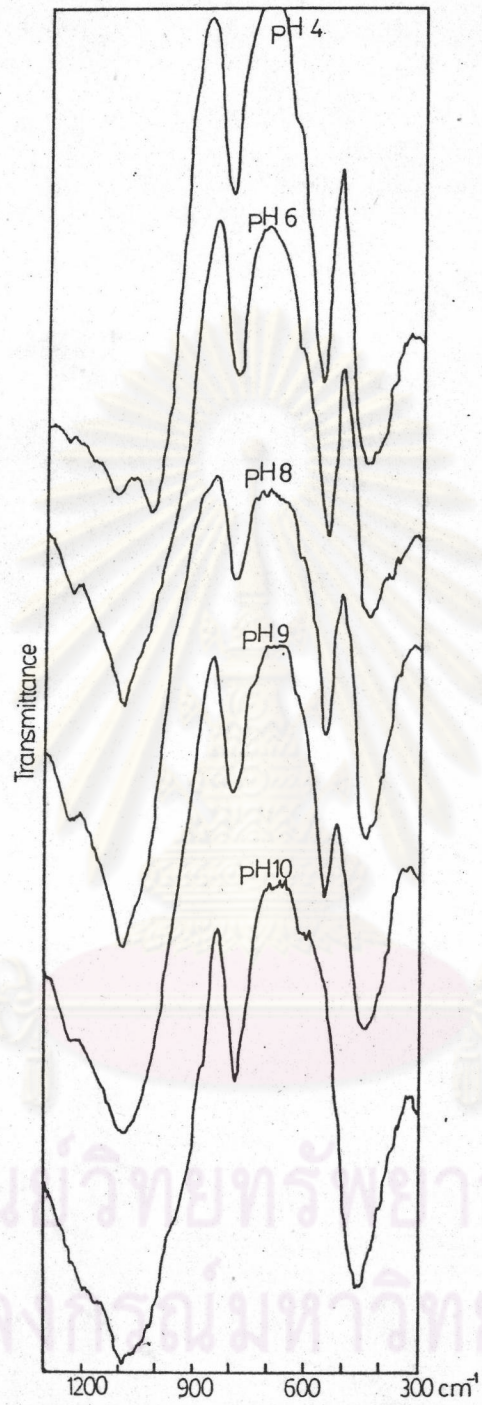


Figure 4.3.25 IR spectra of product crystals for Si/Al mole ratio 400 at various pH

symmetric stretching mode of external linkages. But double ring external linkages bands were only found in the case of pH 8 and 10, they illustrated that at these two pHs, external structure of product crystals had completely developed and at the others were not complete. And IR spectra (fig.4.3.24) of Si/Al mole ratio 200 gave the same results as Si/Al mole ratio 100.

In the case of Si/Al 400, fig.4.3.25 showed IR spectra at various pH, the product crystals from all pH had completely developed of primary building unit TO_4 frameworks and there was the appearance of external linkage. But at $500-650\text{ cm}^{-1}$, double ring external linkage bands only appeared clearly at pH 4,6,8, and 9. They showed that only at these mentioned pH, the crystals were well developed ZSM-5 zeolites so that these were optimum conditions.

4.3.4 Chemical element analysis

Table 4.1, No.4.3.4 showed the results from AA for the study of pH of mixing solutions.

At Si/Al mole ratio 2, real Si/Al mole ratios did not change when pH changed except at pH 12 so that at high pH, silicon could incorporated in aluminosilicate frameworks more than the lower pH.

At Si/Al mole ratios 100, 200 and 400, real Si/Al mole ratios would rather constant in each mole ratio and increased when mole ratios increased so that in this case pH was no effect on real Si/Al mole ratio.

When all the results were compiled together, they showed that low Si/Al mole ratio (2) was not suitable for ZSM-5 synthesis. At Si/Al 100 and 200, optimum pH were 10 and 8, respectively. And from product crystals at Si/Al mole ratio 400, it was shown that acidic pH (4-6) could used to prepare ZSM-5 zeolites and the most optimum pH for ZSM-5 synthesis in this case was pH6.

Table 4.1 The results from chemical element analysis by Atomic Absorption Spectroscopy

No.	Titles of effects	Preparation conditions	%Si	%Al	Real Si/Al ^a mole ratio
4.1.4	Chemical Compositions of Crystals	Si/Al mole- 20	22.42	4.57	4.72
		ratio 40	27.00	2.65	9.79
		100	30.69	2.07	14.25
		140	33.24	1.72	18.57
4.2.4	Initial Pressure in Crystal Synthesis (Si/Almole ratio 140)	P.= 1 atg.	31.36	1.98	15.22
		P.= 3 atg.	33.24	1.72	18.57
		P.= 5 atg.	35.98	2.60	13.30
4.3.4	pH of Mixing Solution	Si/Al=2, pH6	9.37	19.11	0.47
		, pH8	8.70	17.90	0.47
		, pH10	7.09	14.39	0.47
		, pH12	12.58	15.58	0.78
		Si/Al=100, pH6	41.17	2.20	17.98
		, pH8	48.78	2.17	21.60
		, pH10	45.17	2.22	19.55
		, pH12	34.95	2.18	15.40
		Si/Al=200, pH6	31.84	1.29	23.71
		pH8	30.04	1.34	21.54
		pH10	36.26	1.41	24.71
		pH12	32.53	1.43	21.86

Table 4.1 The results from chemical element analysis by Atomic Absorption Spectroscopy (continued)

No.	Titles of effects	Preparation conditions	%Si	%Al	Real Si/Al mole ratio
		Si/Al=400, pH4	34.86	1.06	31.60
		, pH6	53.60	0.86	59.89
		, pH8	48.12	0.76	60.84
		, pH9	33.31	1.03	31.07
		, pH10	37.38	0.86	41.76
4.4.4	Temperature retes in crystal synthesis (Si/Almole ratio140)	<u>heating rate,time</u> ^b (°C/min)			
		1.6 0:43.5	32.78	2.07	15.22
		1.6 1:03	32.56	1.99	15.71
		1.6 1:21	33.33	2.41	13.29
		1.6 3:51	32.77	1.94	16.89
		1.6 5:30	31.99	2.01	15.30
		1.2 0:43.5	33.41	2.15	14.93
		1.2 1:03	30.70	1.99	14.83
		1.2 1:21	30.89	2.07	14.34
		1.2 3:51	33.46	2.04	15.76
		1.2 5:30	30.28	1.94	15.00
		2.0 0:43.5	33.91	1.90	17.15
		2.0 1:03	32.66	1.90	16.52
		2.0 1:21	31.69	1.89	16.11
		2.0 3:51	27.64	3.84	6.90
		2.0 5:30	29.10	3.96	7.06

Table 4.1 The results from chemical element analysis by Atomic Absorption Spectroscopy (continued)

No.	Titles of effects	Preparation conditions	%Si	%Al	Real Si/Al mole ratio
4.5.4	Temperatures and Times in calcination process (Si/Almole ratio=140)	Temp.=540°C, time=3.5 hr.	31.99	2.01	15.30
		before calcined	31.10	2.09	14.30

^a real Si/Al mole ratio = $(\text{Si}/\text{Al})(\text{MW}.\text{Al}/\text{MW}.\text{Si}) = 0.9609(\text{Si}/\text{Al})$

^b crystal synthesized time

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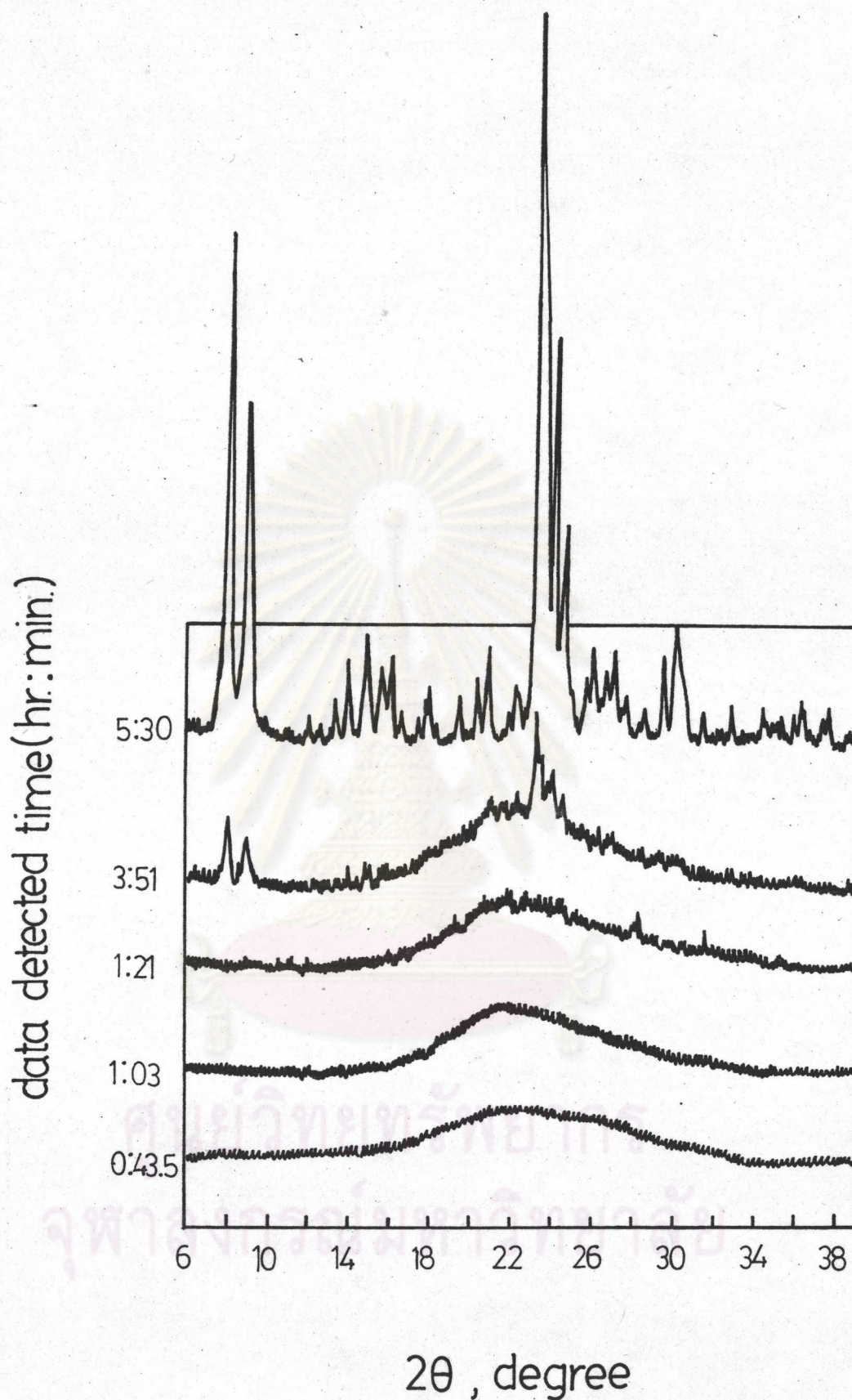


Figure 4.4.1 XRD patterns of product crystals for heating rate 1.6 °C/min. at various crystallization time in the crystallizer

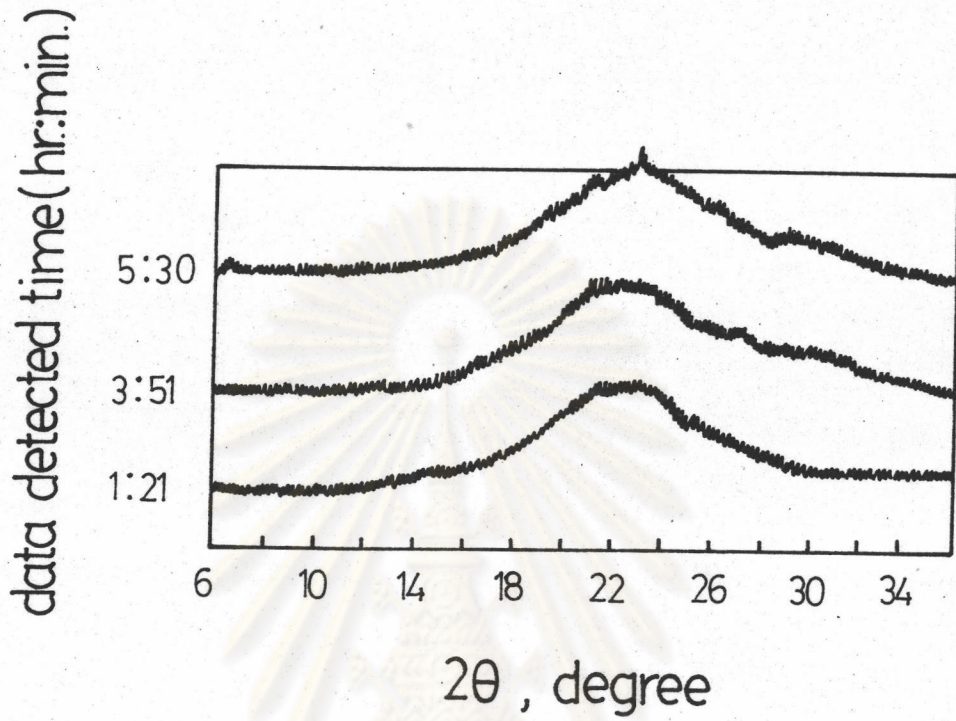


Figure 4.4.2 XRD patterns of product crystals for heating rate $1.2^\circ\text{C}/\text{min}$. at various crystallization time in the crystallizer

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4.4 Temperature rates in crystal synthesis.

The guide line for this study was clearly shown in fig. 3.4 of chapter III, the heating rate which used in this study were 1.2, 1.6, and 2.0^o C/min.

4.4.1 Characterization of product crystals by crystallinity analysis.

By using the first heating rate at 1.6^oC/min. to study the crystal formation at various temperatures and times of crystal synthesis in crystallizer. When sample was detected at 43.5 min., XRD data (fig. 4.4.1) showed no peak of crystal, therefore in this stage, the products were amorphous as same as at the sample-detected time 1 hr. and 3 min. and 1 hr. and 21 min. Until it took the time 3 hr. and 51 min. (by heating up from room temperature with heating rate 1.6^oC/min to 160^o, then changed heating rate to be 12^oC/hr.), XRD-pattern showed the appearance of ZSM-5 crystal in low level. It was illustrated that, at this time, the ZSM-5 crystals still were incomplete developed. Therefore, if there were more time and higher temperatures, the product crystals would have been complete developed. It took the time about 5 hr. and 30 min., XRD-pattern showed the complete pattern of ZSM-5 zeolite with very high crystallinity. Consequently, in crystal synthesis of ZSM-5 zeolite, at heating rate 1.6^oC/min., the optimum time in crystallizer was about 5 hr. and 30 min. which could gave complete developed of product crystals more than the other times.

For first heating rate at 1.2^oC/min. The results of XRD-patterns of various sample detected times weref shown in fig. 4.4.2. All of XRD-pattern showed that product-crystals at various sample-detected times were amorphous, there was no ZSM-5 zeolite crystal in the products. For this reason, the heating rate constant 1.2^oC/min was not optimum for ZSM-5 synthesis.

Figure 4.4.3 showed XRD-patterns of product crystals at various sample-detected times in the case of first heating rate $2.0^{\circ}\text{C}/\text{min}$. When times passed for 43.5 min, 1 hrd. and 3 min., and 1 hr. and 21 min, XRD-patterns illustrated that product crystals were amorphous, after time passed for 3 hrd. and 51 min. (heating up from 190°C with heating rate $12^{\circ}\text{C}/\text{hr.}$), the XRD-pattern showed that there were zeolite crystals (not ZSM-5) mixed in product crystal and the crystallinity was very high. It was shown that at this time, crystals had complete developed, also with at the time 5 hr. and 30 min. When these two results from XRD-patterns were compare with each other, the crystallinity of product crystals at time 3 hr. and 51 min. was higher than that one at time 5 hr. and 30 min. It was suggested that after the time past for 3 hr. and 51 min., some of zeolite crystals were destroyed by high temperature and pressure, so the crystallinity was decreased.

When all results from various heating rates were compared with each other for the most optimum heating rate which was used in ZSM-5 synthesis, it was found that heating rate $1.6^{\circ}\text{C}/\text{min}$. was the most optimum heating rate constant.

4.4.2 External structure analysis by scanning electron microscope.

Figure 4.4.4 was the SEM-photograph of crude crystals which were detected the sample before synthesis in the crystallizer, the products were amorphous. They were small granules with size about $0.1\ \mu\text{m}$. There was no ZSM-5 crystal in the products.

For the study of effect of temperature rate on structure of zeolite, at the first heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 43.5 min., 1 hr. and 3 min, and 1 hr. and 21 min, SEM-photographs were shown in figs. 4.4.5, 4.4.6 and 4.4.7 respectively. These three results were the same, the products were amorphous form which like small

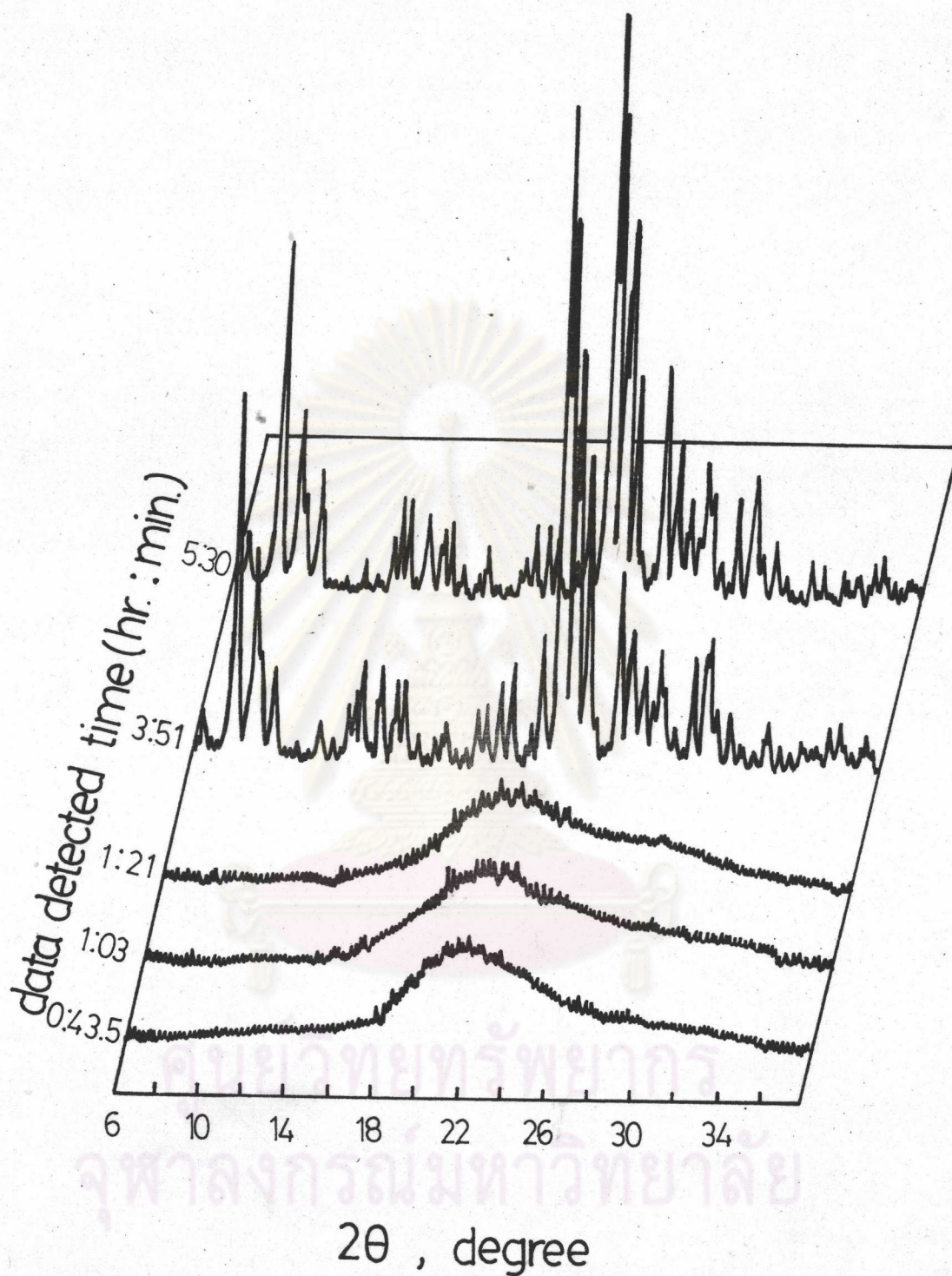


Figure 4.4.3 XRD patterns of product crystals for heating rate 2.0 °C/min. at various crystallization time in the crystallizer

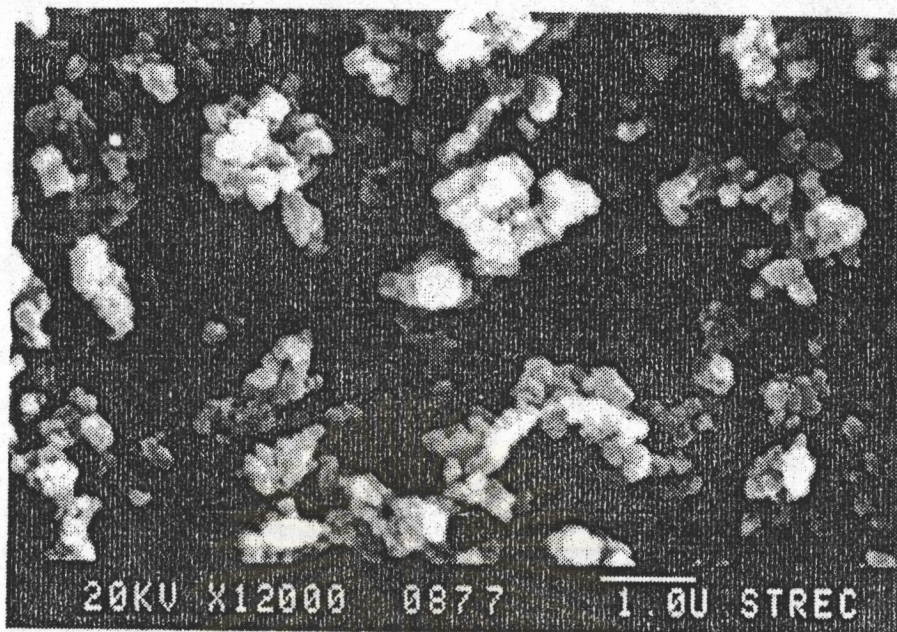


Figure 4.4.4 SEM photomicrograph of crude crystals before synthesis in the crystallizer.

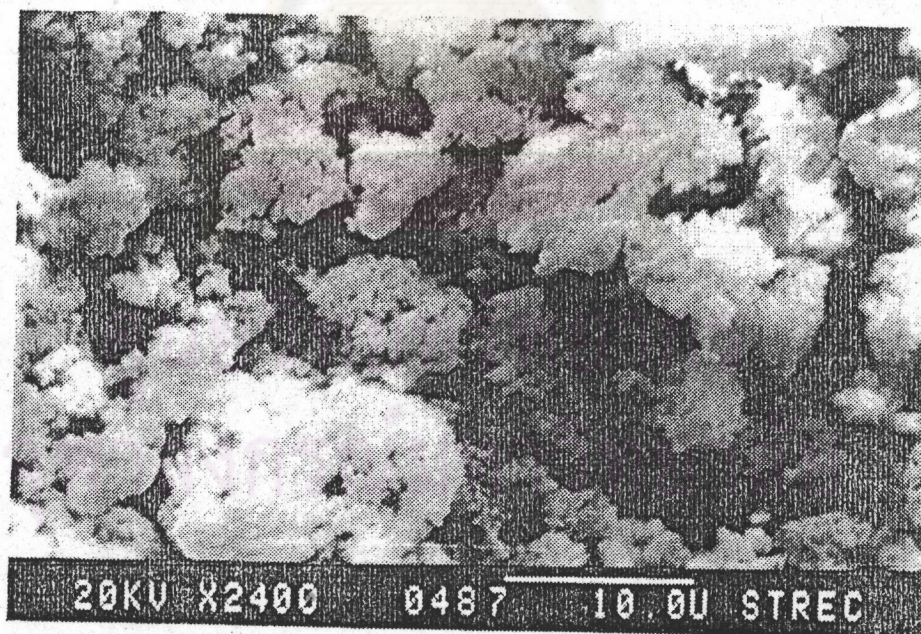


Figure 4.4.5 SEM photomicrograph of product crystals for heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 43.5 min.

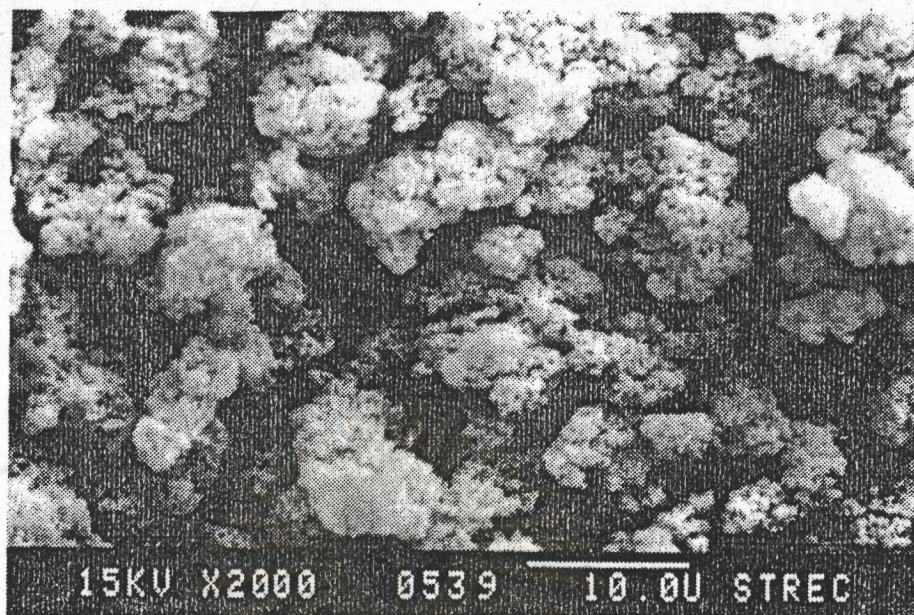


Figure 4.4.6 SEM photomicrograph of product crystals for heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 3 min.

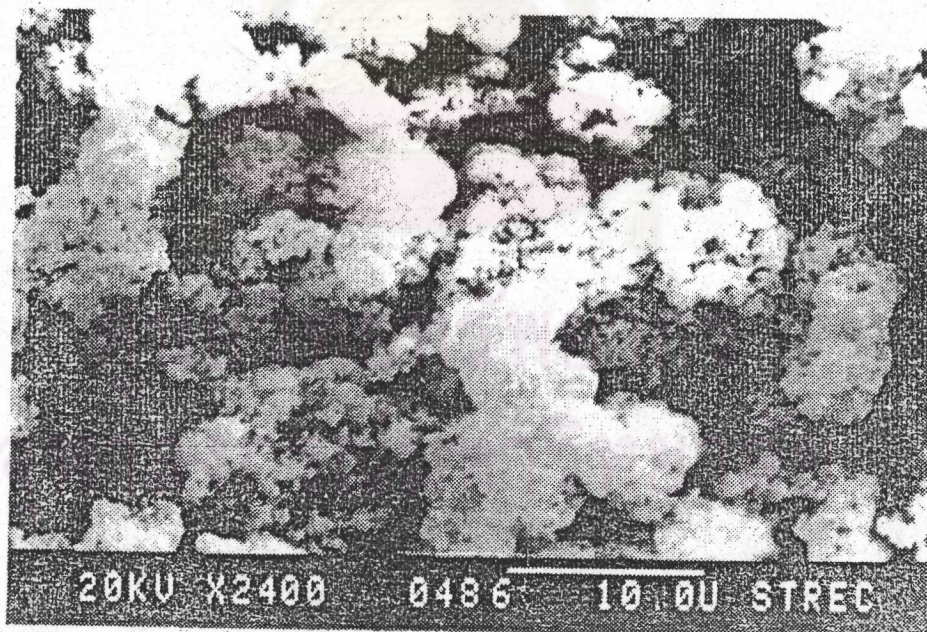


Figure 4.4.7 SEM photomicrograph of product crystals for heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 21 min.

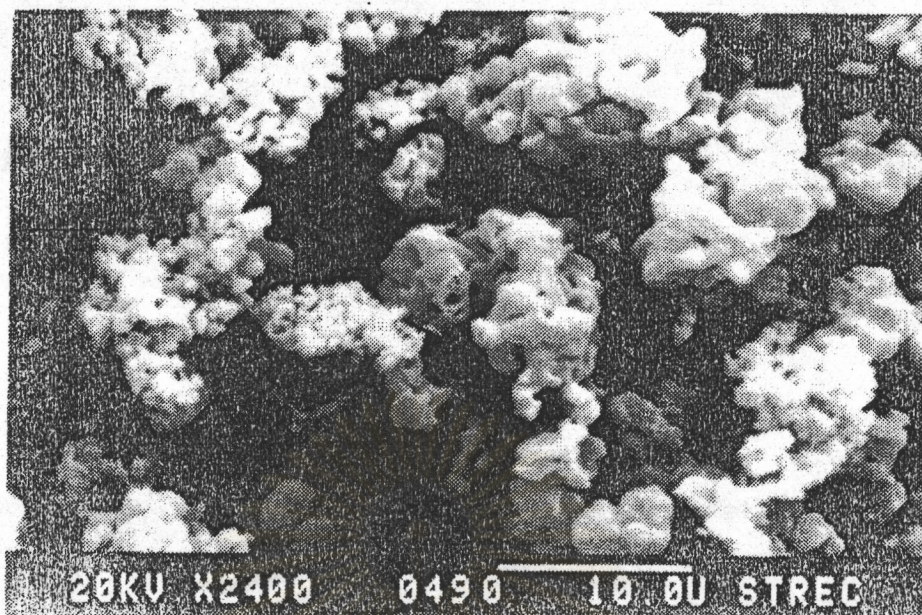


Figure 4.4.8 SEM photomicrograph of product crystals for heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 3 hr. and 51 min.

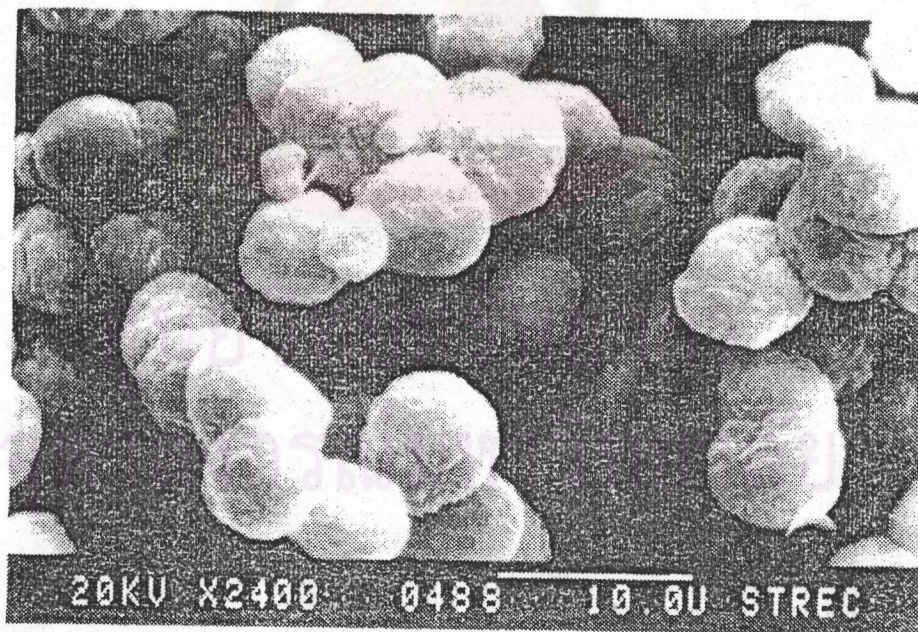


Figure 4.4.9 SEM photomicrograph of product crystals for heating rate $1.6^{\circ}\text{C}/\text{min}$ and sample-detected time 5 hr. and 30 min.

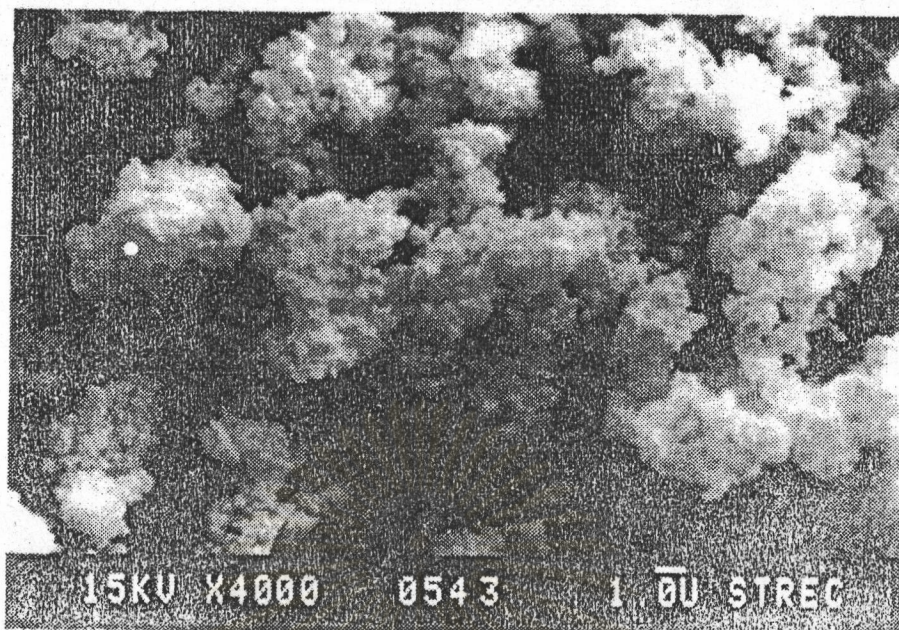


Figure 4.4.10 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 43.5 min.

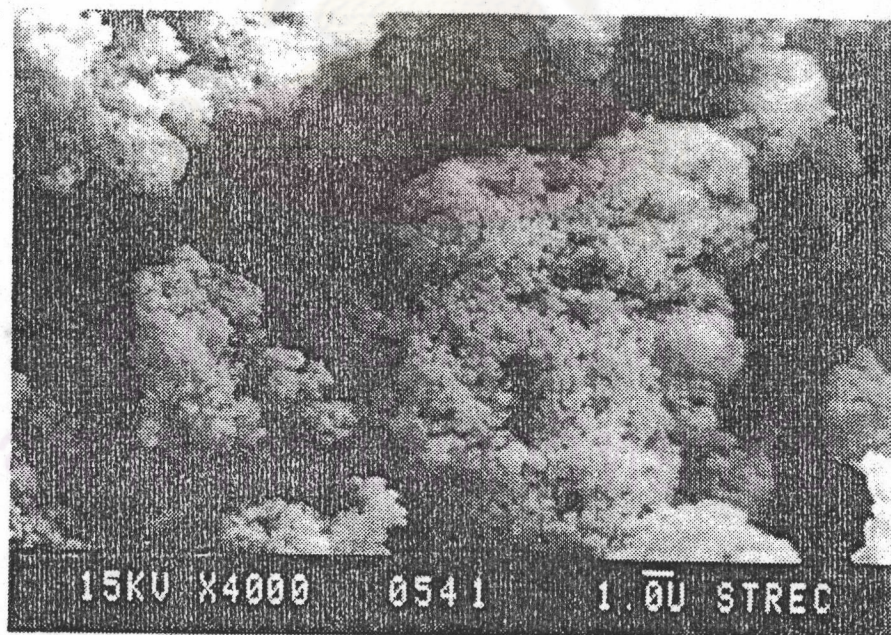


Figure 4.4.11 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 3 min.

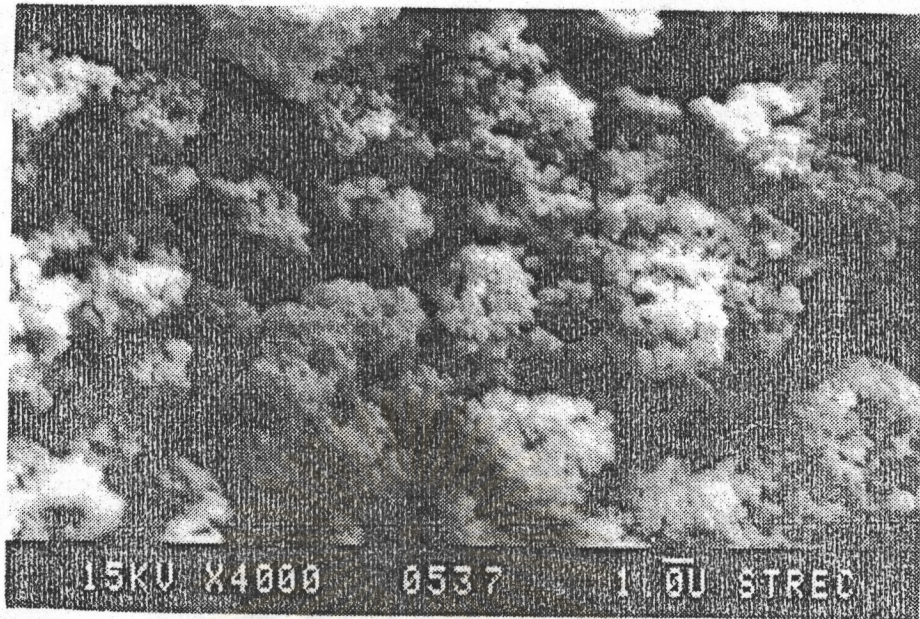


Figure 4.4.12 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 21 min.

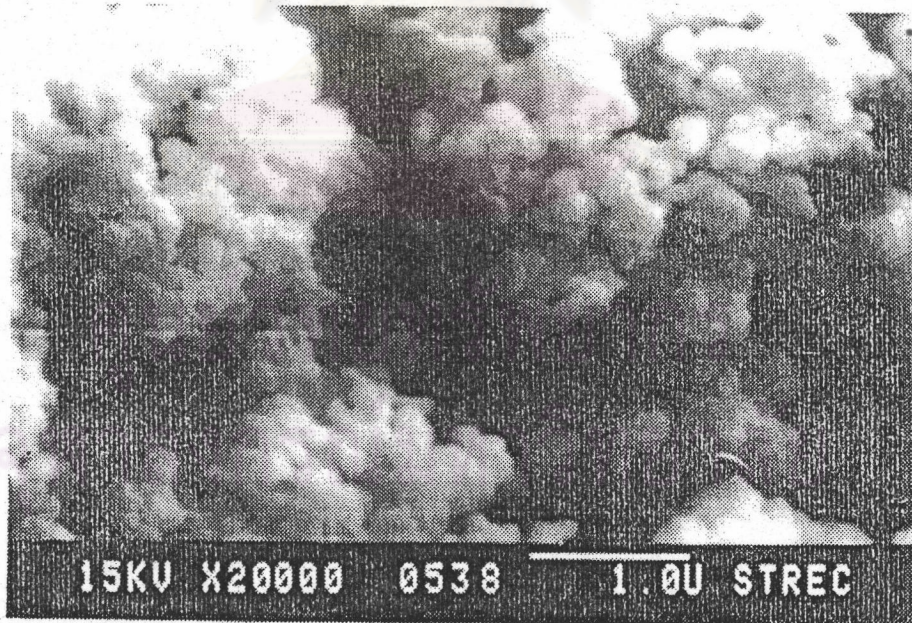


Figure 4.4.13 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 21 min.

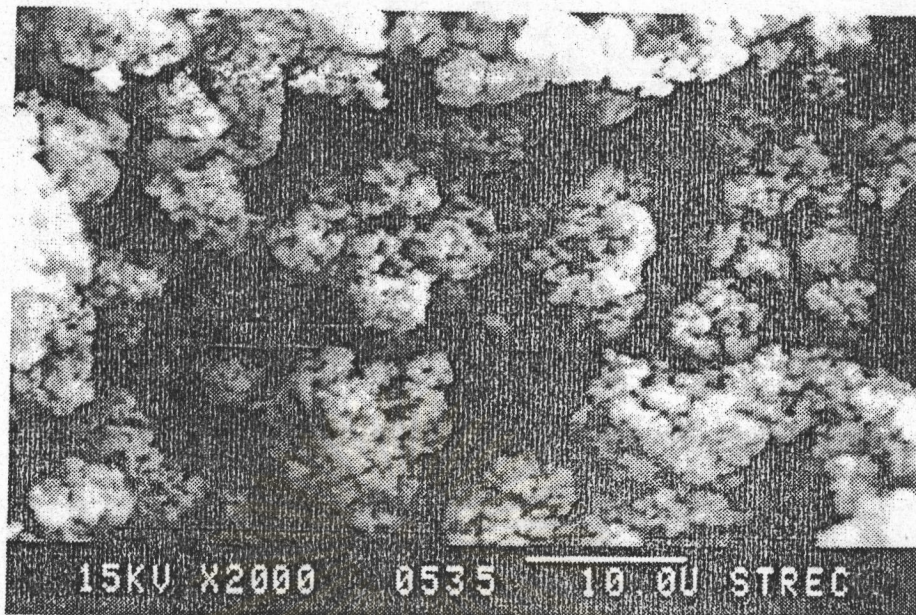


Figure 4.4.14 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 3 hr. and 51 min.

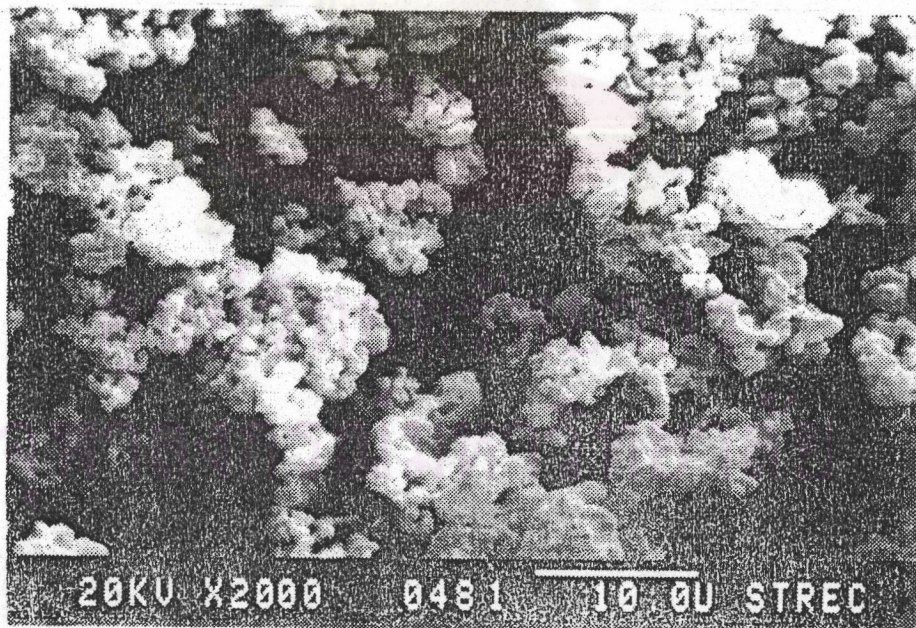


Figure 4.4.15 SEM photomicrograph of product crystals for heating rate $1.2^{\circ}\text{C}/\text{min}$ and sample-detected time 5 hr. and 30 min.

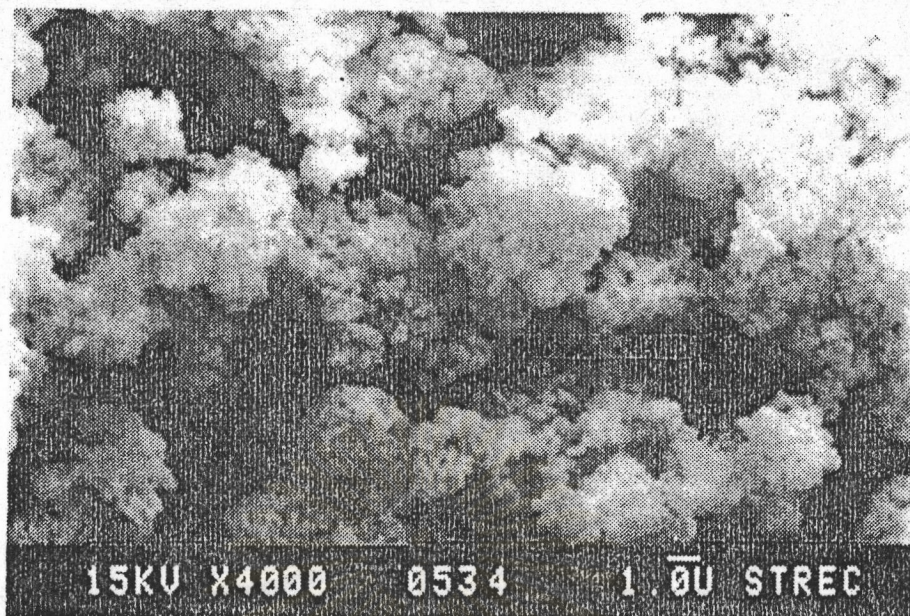


Figure 4.4.16 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 43.5 min.

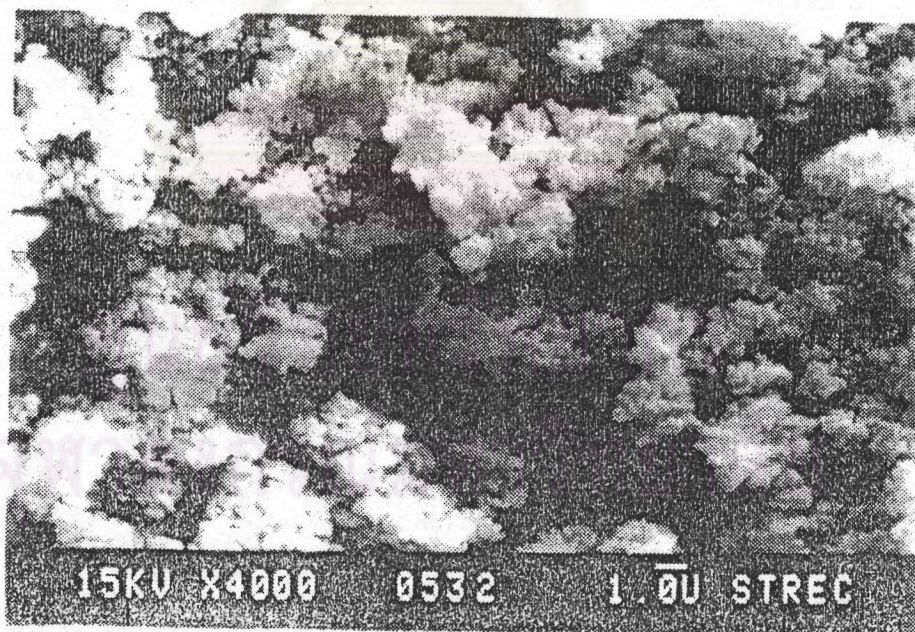


Figure 4.4.17 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 3 min.

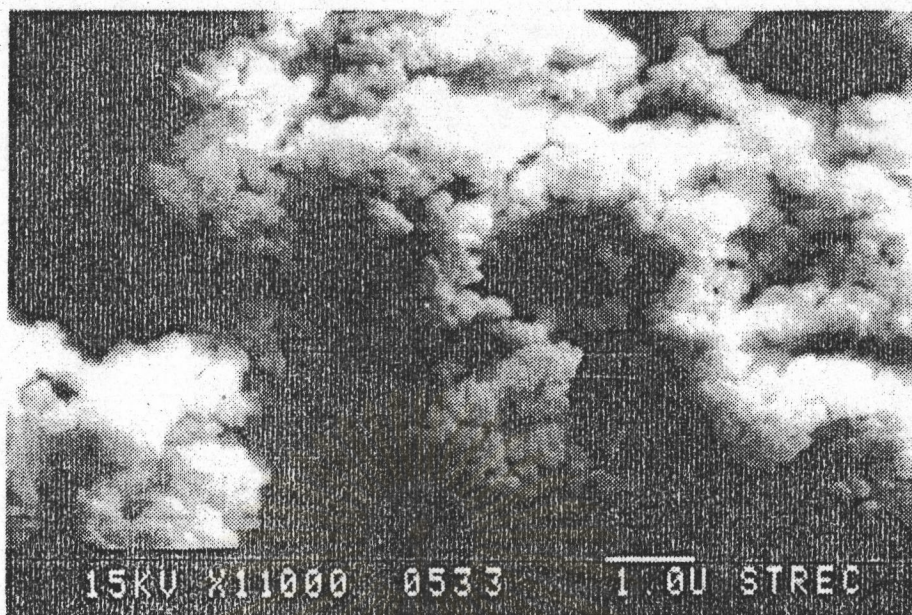


Figure 4.4.18 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 3 min.



Figure 4.4.19 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 1 hr. and 21 min.

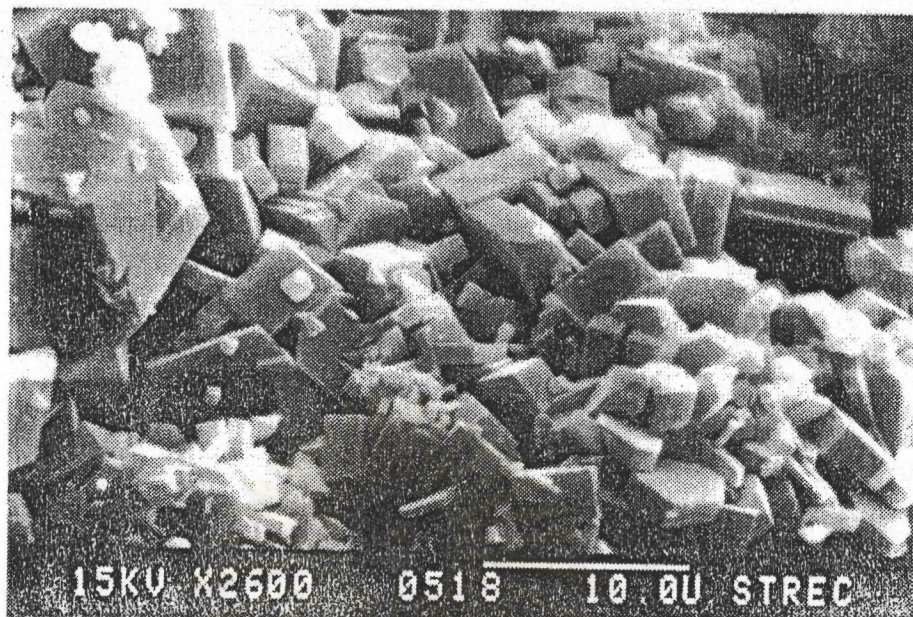


Figure 4.4.20 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 3 hr. and 51 min.

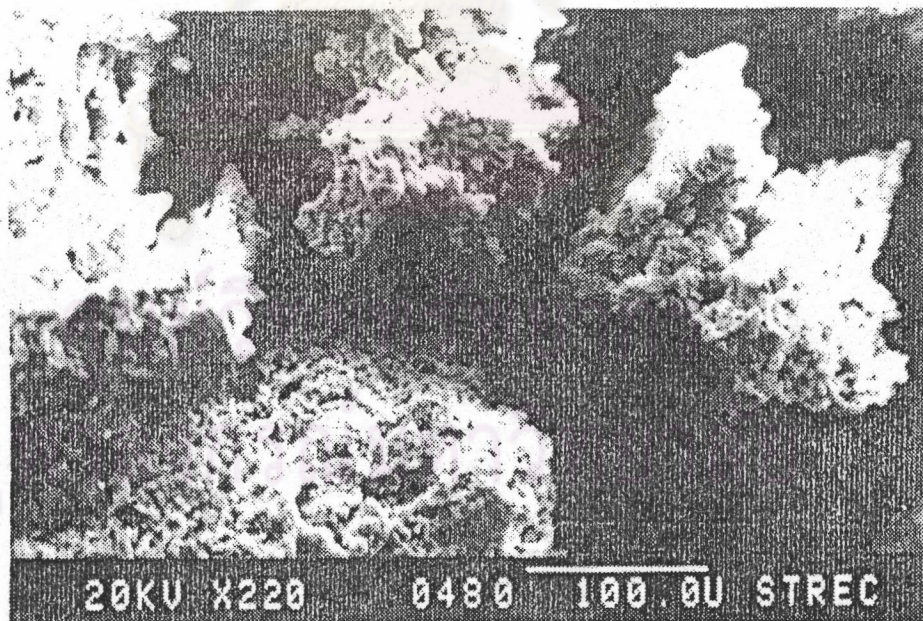


Figure 4.4.21 SEM photomicrograph of product crystals for heating rate $2.0^{\circ}\text{C}/\text{min}$ and sample-detected time 5 hr. and 30 min.

granules, and no ZSM-5 crystal contained in the products. When detecting the sample at the time 3 hr. and 51 min., the result was shown in fig. 4.4.8, there were spherical form of ZSM-5 crystals mixed with amorphous formed products. Therefore, at this time, some crystals had complete developed but more than half of product were still amorphous form. When the products were synthesized in the crystallizer for 5 hr. and 30 min. (fig. 4.4.9), the crystals was 100% ZSM-5, there was no impurity mixed in product crystals. The crystals were well-developed with size about 6 μm . It was seen that there were same small spherical forms of crystals which showed new-developed crystals. Therefore, at heating rate 1.6 $^{\circ}\text{C}/\text{min}$., the optimum time which used to synthesis ZSM-5 crystals was 5 hr. and 30 min. at least (for the longer times, there was not studied about them).

At the first heating rate 1.2 $^{\circ}\text{C}/\text{min}$., product crystals were all amorphous even if the time in crystallizer passed for 5 hr. and 30 min., as shown in figs. 4.4.10 - 4.4.15, for the sample-detected times at 43.5 min., 1 hr. and 21 min., 3 hr. and 51 min., and 5 hr and 30 min., respectively. All of products were small granules with size about 0.1-0.2 μm . Therefore, this heating rate constant was not optimum for ZSM-5 synthesis.

For the first heating rate 2.0 $^{\circ}\text{C}/\text{min}$., when time in crystallizer passed 43.5 min., 1 hr. and 3 min., and 1 hr. and 21 min., the results of SEM-photographs were shown in figs. 4.4.16 - 4.4.19, respectively. All products were amorphous forms with size 0.1-0.2 μm . In fig. 4.4.19, at sample detected time 1 hr. and 21 min., it was clearly seen the embryo of crystal. These embryos were spherical forms which still incomplete developed. At the time passed for 3 hr. and 51 min., SEM-photograph of product crystals was shown in fig. 4.4.20, the product crystals were composed with 90% cubic forms and spherical forms

with very different sizes. They were suggested to be ZSM-5 crystals with had fast developed. The results of SEM-photograph of product crystals at sample-detected time 5 hr. and 30 min. was shown in fig. 4.4.21. The products were amorphous forms. From this result, it was concluded that at very high temperature and pressure, the crystal could be destroyed. Consequently, the optimum time in crystal synthesis at heating rate $2.0^{\circ}\text{C}/\text{min}$. was 3 hr. and 51 min.

4.4.3 Functional group analysis

At first heating rate $1.6^{\circ}\text{C}/\text{min}$., the IR spectral of product crystals from various times in crystallizer showed the complete development of TO_4 tetrahedron but external linkages still incomplete developed except at the times 5 hr. and 30 min. they illustrated that the optimum times in crystallizer at this heating rate was 5 hr. and 30 min.

For heating rate $1.2^{\circ}\text{C}/\text{min}$., IR spectra showed that all product crystals had TO_4 tetrahedra frameworks and some external linkages but had not double ring mode of external linkages. Even if the times in crystallizer was increased, external linkages structure of zeolites still incomplete developed, so this heating rate was not ZSM-5 synthesis.

In the case of heating rate $2.0^{\circ}\text{C}/\text{min}$. IR spectra of product crystals at various synthetic time were shown in fig.4.4.24. This figure the complete development of TO_4 tetrahedral frameworks and the increasing of external linkage band when synthetic times were increased. Product crystals developed completely when the synthetic times was 3 hr. and 51 min. but was not ZSM-5 crystallites.

4.4.4 Chemical element analysis

From No.4.4.4 in table 4.1, at various heating rates and synthetic times, all real Si/Al mole ratios were constant except at

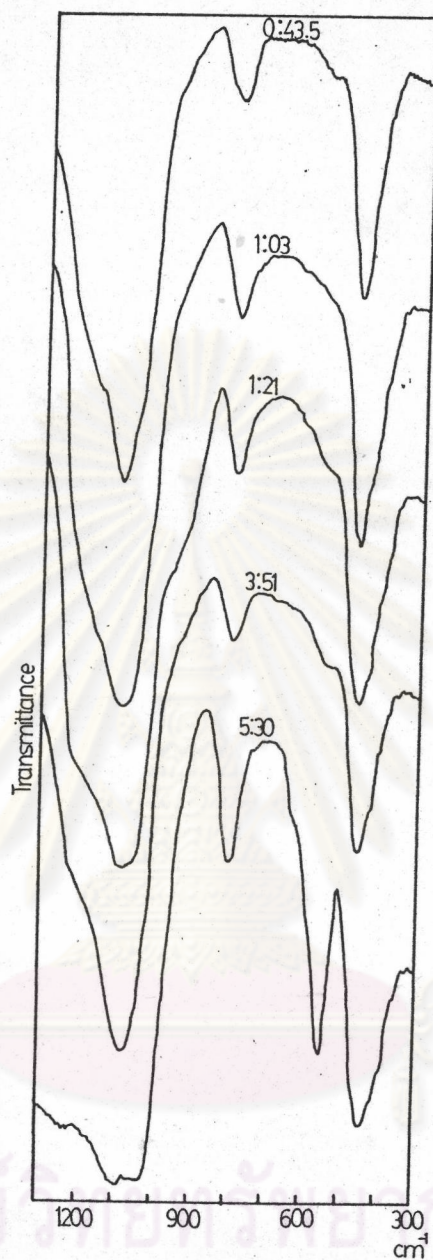


Figure 4.4.22 IR spectra of product crystals for heating rate 1.6 $^{\circ}\text{C}/\text{min.}$ at various crystallization times

heating rate $2.0^{\circ}\text{C}/\text{min.}$ and time 3:51 hr. and 5:30 hr. Therefore, real Si/Al mole ratios almost were not affected by temperature rate in crystal synthesis.

From those mentioned results in sections 4.4.1-4.4.4, all the results showed that the most optimum temperature rates in ZSM-5 synthesis was $1.6^{\circ}\text{C}/\text{min.}$ with the synthetic time 5:30 hr. For heating rate $1.2^{\circ}\text{C}/\text{min.}$, the rate was too low to synthesize these crystals but at heating rate $2.0^{\circ}\text{C}/\text{min.}$, the other types of zeolite crystallites appeared.

4.5 Temperatures and times in calcination process.

In this study, temperatures and times were varied to observe their effects on structure of ZSM-5, crystals.

4.5.1 Characterization of product crystals by crystallinity analysis.

XRD-patterns of product crystals were shown in fig. 4.5.1 From this figure, all XRD-patterns showed clearly that all products were ZSM-5 crystals. When crystallinity of each crystals were compared together, it was found that crystallinity was ordered as follows: crystallinity; before calcined > calcined at 450°C , 3.5 hr. > calcined at 540° , 2.5 hr. > calcined at 540° , 3.5 hr > calcined at 6340° , 3.5 hr.

Therefore, when temperature and time in calcination process were increase, the result was the decreasing of product crystallinity in small amounts. For those reasons, it was concluded that temperature and time in calcination process had a little effect on crystallinity of ZSM-5 crystals.

4.5.2 External structure analysis by scanning electron microscope

SEM-photographs of product crystals at various temperatures

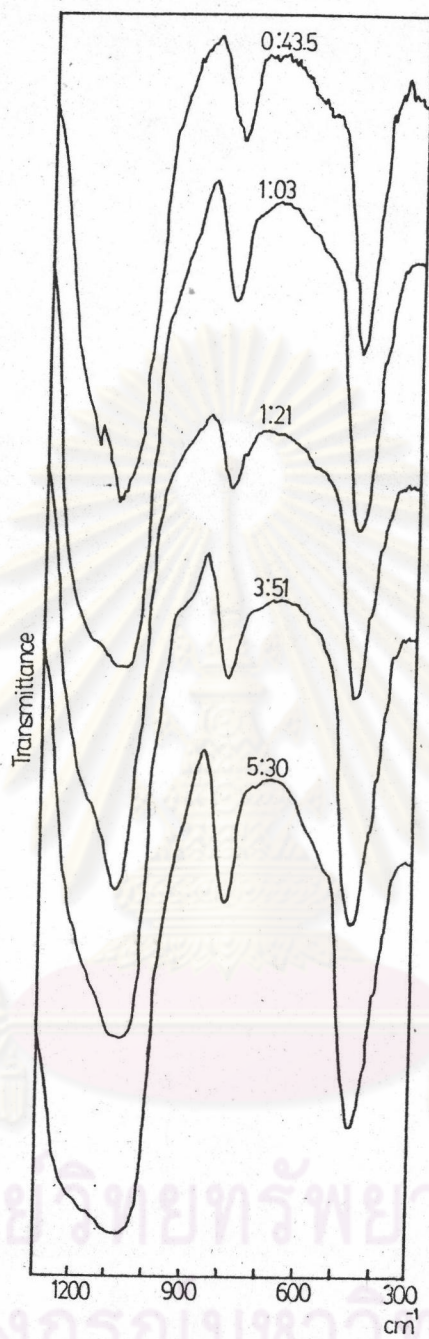


Figure 4.4.23 IR spectra of product crystals for heating rate 1.2 °C/min. at various crystallization times

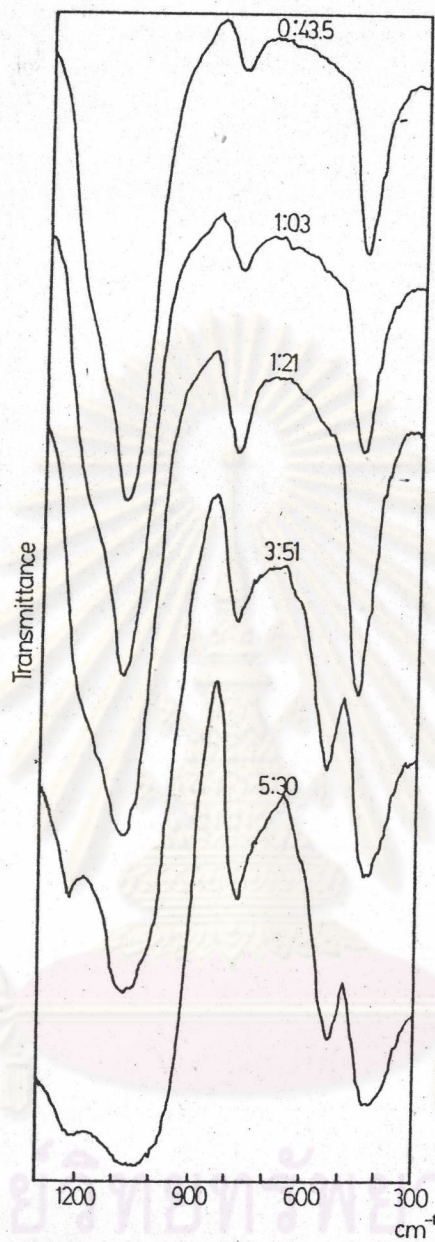


Figure 4.4.24 IR spectra of product crystals for heating rate 2.0 °C/min. at various crystallization times

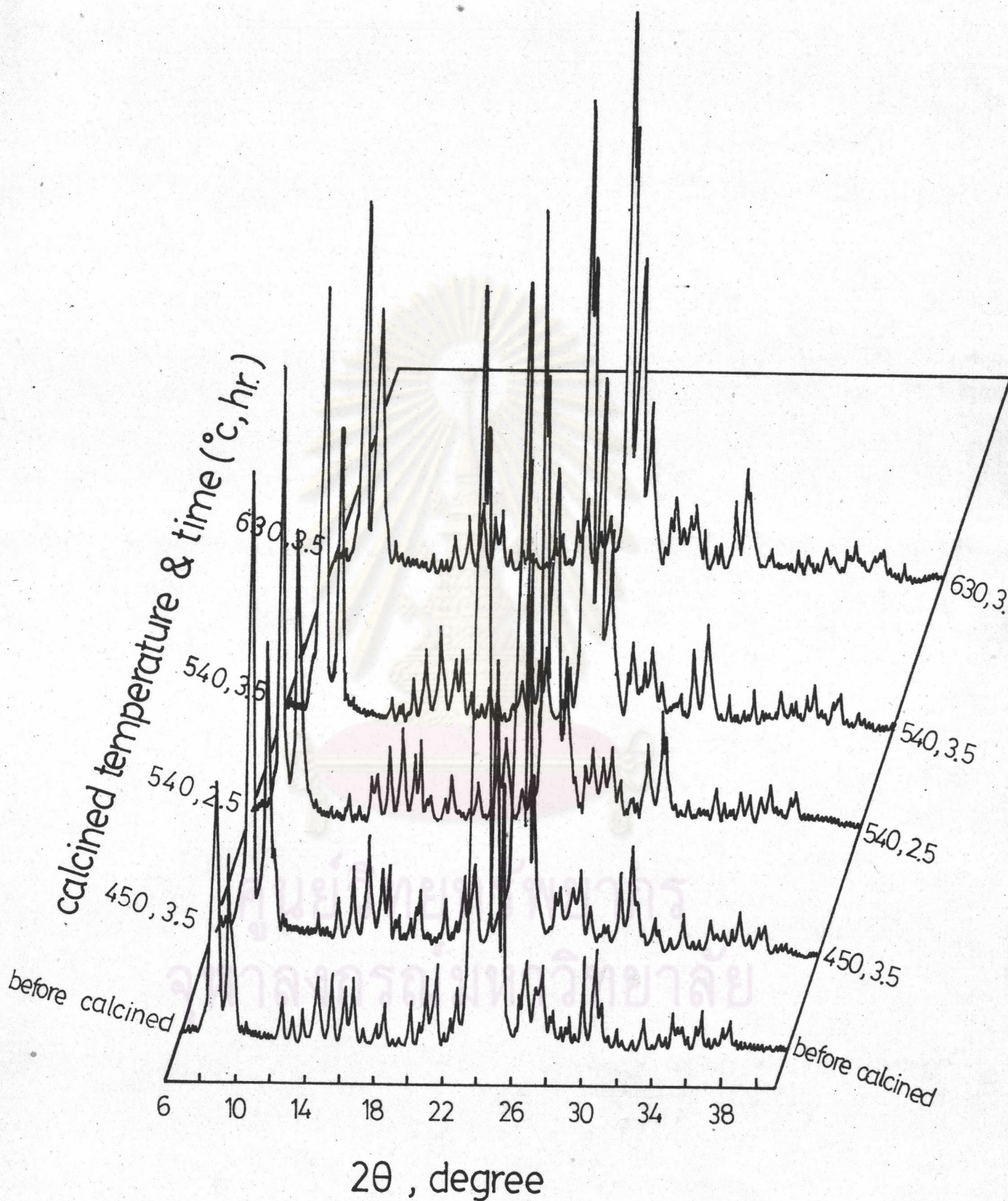


Figure 4.5.1 XRD patterns of product crystals at various temperatures and times in calcination process

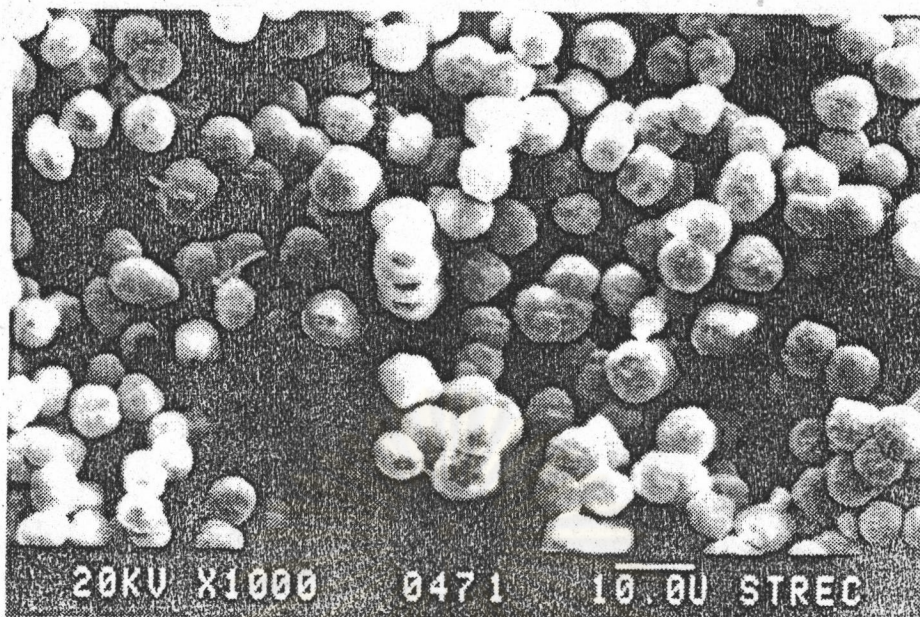


Figure 4.5.2 SEM photograph of product crystals before calcination

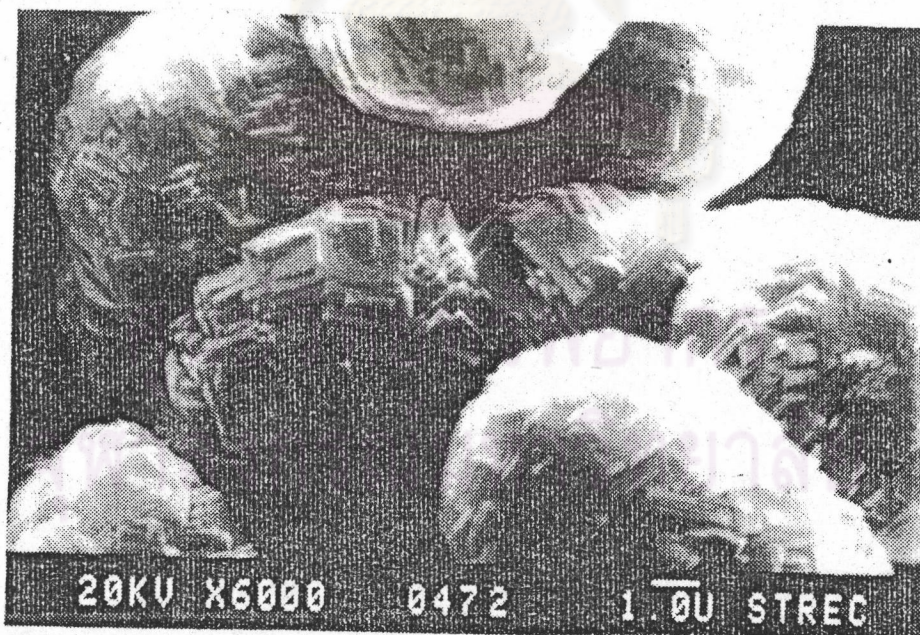


Figure 4.5.3 SEM photograph of product crystals before calcination

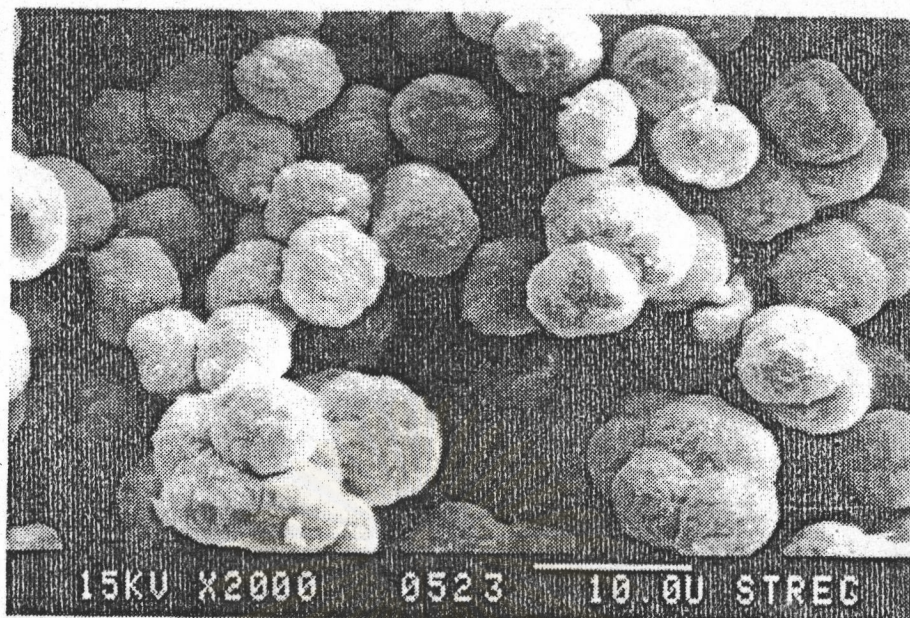


Figure 4.5.4 SEM photograph of product crystals at calcined temperature 450 °C and times 3.5 hr.

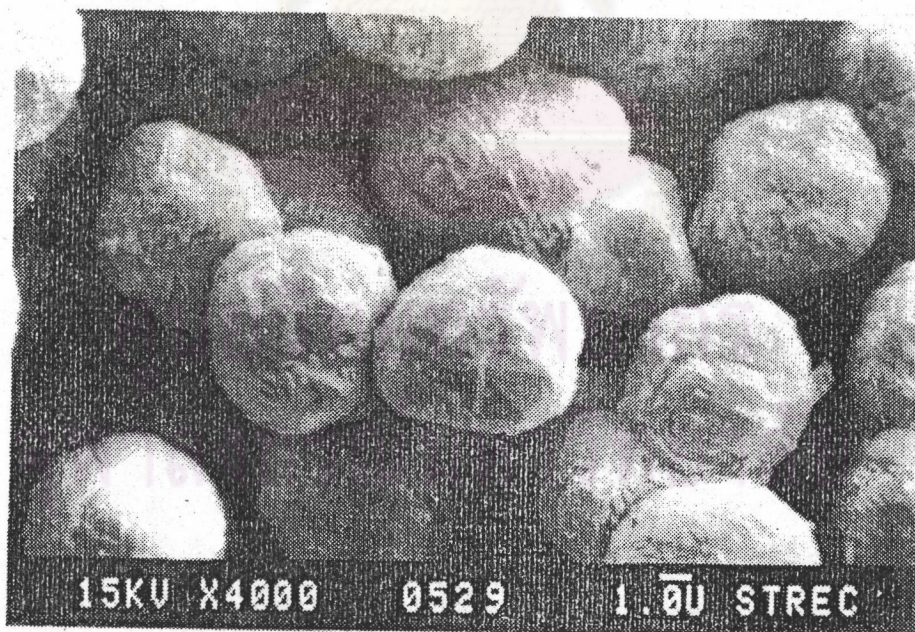


Figure 4.5.5 SEM photograph of product crystals at calcined temperature 540 °C and times 1.5 hr.



Figure 4.5.6 SEM photograph of product crystals at calcined temperature 540 °C and times 2.5 hr.



Figure 4.5.7 SEM photograph of product crystals at calcined temperature 540 °C and times 2.5 hr.

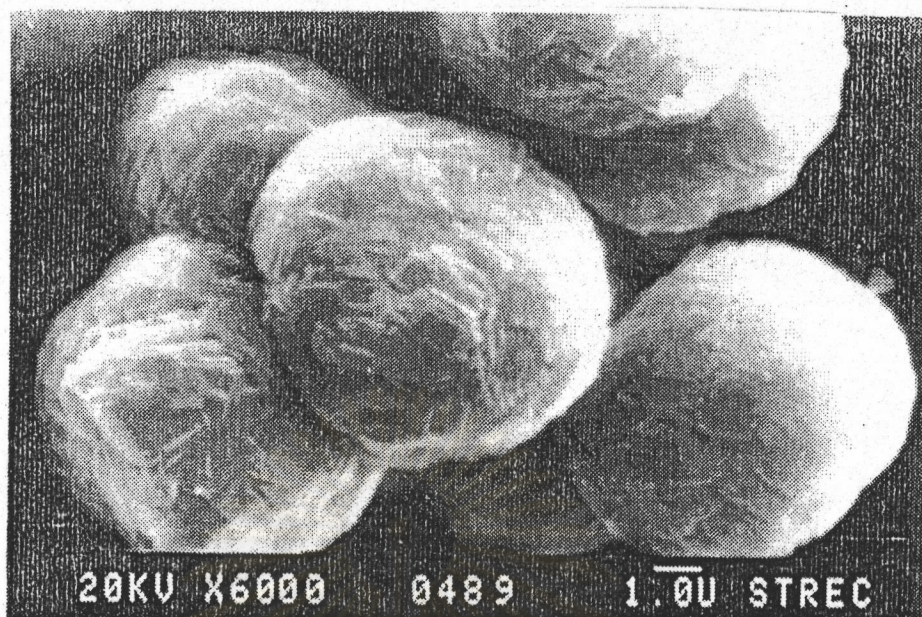


Figure 4.5.8 SEM photograph of product crystals at calcined temperature 540 °C and times 3.5 hr.



Figure 4.5.9 SEM photograph of product crystals at calcined temperature 630 °C and times 3.5 hr.

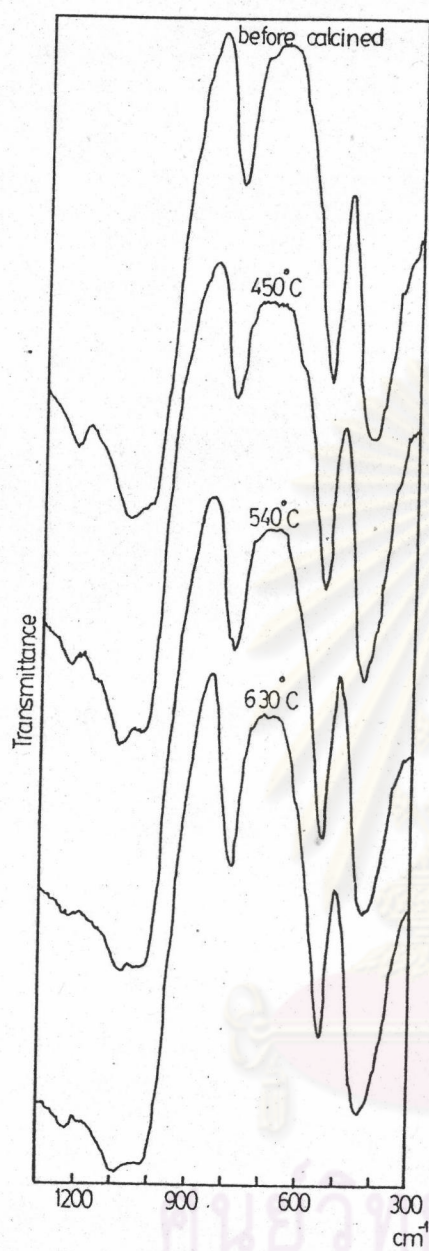


Figure 4.5.10 IR spectra of product crystals

at various calcined temperatures

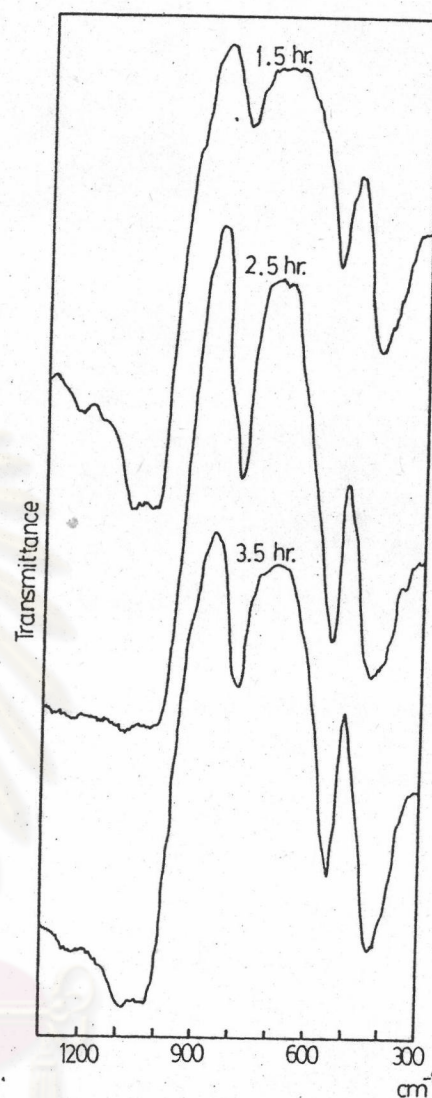


Figure 4.5.11 IR spectra of product crystals at various calcined times

and times in calcination process were shown in figs. 4.5.2 - 4.5.9. All of SEM-photographs showed clearly that product crystals were 100% ZSM-5 crystals. These crystals had spherical form with crude surface. In fig. 4.5.3, with multiplicity of 6,000, these were ZSM-5 crystals of products which were not calcined. It was clearly seen that the crystal was composed with small sheets to form spherical crystal with size about 6-8 μm .

For the product crystal at calcined temperature and time 450°C and 3.5 hr., respectively, SEM-photograph (fig. 4.5.4) was the same as the one of before-calcined product crystals. All crystals were ZSM-5 zeolites with size about 6-8 μm and spherical form.

The results of SEM-photomicrographs at 540°C for 1.5, 2.5, and 3.5 hr. and 630°C for 3.5 hr. were shown in figs. 4.5.5 - 4.5.9, respectively. All results were as same as the results of product crystals which were not calcined and that one at 450°C for 3.5 hr.

It was suggested that the analysis of external structure of crystals by SEM at various conditions in calcination process could not give the exact conclusion because of the rigid of external structure of ZSM-5 zeolites. Therefore, in this case, other analytical methods would be brought to compile results with each others.

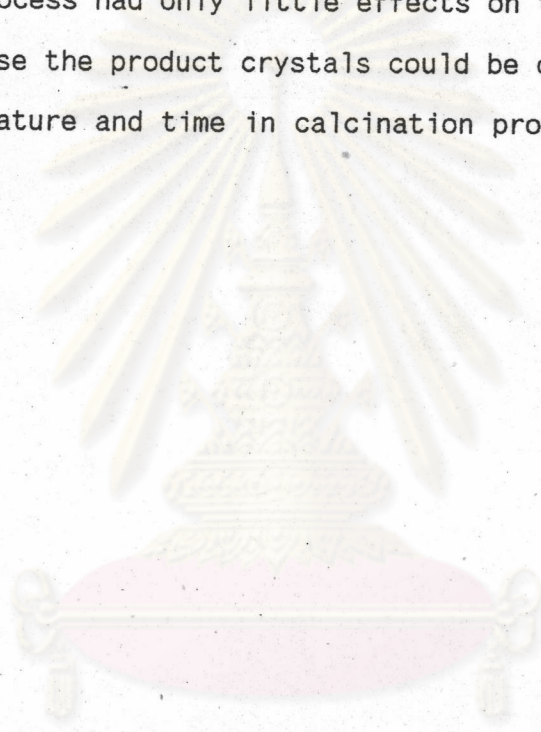
4.5.3 Functional groups analysis

IR spectra of the product crystal from the study of temperatures and times in calcination process were shown in figs. 4.5.10 and 4.5.11. In these two figures, all the results were same, IR spectra showed the bands of asymmetric stretching and T-O bending of internal tetrahedra and symmetric stretching and double ring mode of external linkages. These bands illustrated that the product crystals were well developed ZSM-5 crystals. So it would be concluded that this factor had a little effects on functional groups of zeolite crystallites.

4.5.4 Chemical elements analysis

The results from AA were shown in No. 4.5.4, table4.1. They illustrated that real Si/Al mole ratios did not change when temperatures and times in calcination process were changed. So, temperatures and times in calcination process had no or little effects on the structure of ZSM-5 crystallites.

Therefore, it was concluded that temperatures and times in calcination process had only little effects on the structure of pentasil zeolites because the product crystals could be destroyed by thermal. The optimum temperature and time in calcination process were 540 °C and 2.5 hr.



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