

CHAPTER VII
MICROWAVE PREPARATION OF LI-ZEOLITE DIRECTLY FROM
ALUMATRANE AND SILATRANE

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7.1 Abstract

Li-zeolite was successfully synthesized in a one-step sol-gel process and microwave technique using silatrane and alumatrane as precursors and lithium hydroxide as the hydrolytic agent. Due to exact nature of microwave in interaction with materials, Li-zeolite was produced at ~ 70 °C which was lower than that observed from DSC. Perfect crystalline zeolite, EDI type zeolite, was obtained at 90 °C after heating for 60 min while ABW type zeolite was produced after heating for 300 minutes at 110 °C. Si/Al ratio of synthesized product increased with increasing temperature and a higher packing density product was generated. At Si/Al ratio of 1, $\text{Li}_2\text{O}/\text{SiO}_2$ ratio of 3 and microwave heating temperature of 110 °C, a mixture of EDI and ABW was found most of the time. Changing Si/Al loading ratio highly influenced the morphology of the synthesized product even in the same product type. With increasing Al-loading, more irregular morphology products and smaller Si/Al ratio of synthesized product were obtained. Changing $\text{Li}_2\text{O}/\text{SiO}_2$ ratio, led to changes in the unit cell structure and crystal morphology. Lowering the $\text{Li}_2\text{O}/\text{SiO}_2$ ratio to one, produced FAU type zeolite. The thermal stability of EDI and ABW were very low while that of FAU was higher which might come from the effect of low ring strain construction of FAU.

Keywords: Alumatrane, Silatrane, Microwave technique, Sol-gel process, and Li-zeolite

7.2 Introduction

Microwave heating techniques are now widely used in many applications in chemical research including organic/inorganic synthesis due to their fast and energy-efficient techniques and avoiding competitive reactions in known processes¹. By combining hydrothermal crystallization with microwave heating technique, a new synthesis method has been developed, giving smaller and more uniform particles in a shorter time²⁻³. Hence, it has been used in converting silicate or aluminosilicate gels to crystalline products.

Normally, final product structures and types depend on the gel compositions. The type of alkali cations is one of the major parameters. They appear to regulate the transformation of the amorphous gel into either crystalline zeolite or other silicate phase by changing the aluminosilicate dissolution rate, which affect the degree of polymerization of silicate or aluminosilicate anion in solution⁴. Moreover, changing the alkali cations also affects the structure of the amorphous gel and changes the stability of some of the synthesized products under hydrothermal conditions⁵. However, there are some papers reported that cations do not have a structure-directing role, stabilizing soluble silicate or aluminosilicate anion and void filling during crystallization⁴⁻⁵. Alkalinities also influence the gel formation⁶ and remarkably contribute to the dissolution step of silicate and aluminate anion in the gel⁷. Because of effecting on the pH, they can also change the silicate chemistry thereby playing a critical role in determining what product is formed⁸. At high pH values, aluminate is less soluble and therefore crystallization of aluminosilicate is favored.

Based on our previous results, silatrane and alumatrane can be successfully used as precursors for the sol-gel process by using sodium hydroxide or sodium chloride as hydrolytic agent⁹. The hydrolysis rate of sodium hydroxide system is two times faster than that of sodium chloride system. However, in making zeolites by hydrothermal treatment, a zeolite product is obtained only from the gel made from sodium hydroxide system only due to the role of hydroxyl group in dissolving the gel at the crystallization step. By using these atranes, pure ANA and GIS type zeolites were obtained at lower temperature and shorter time. Perfect crystal of LTA

type or Na A zeolite is obtained at different Si:Al loading ratio from GIS and ANA¹⁰. Moreover, Na₂O:SiO₂ loading ratio affects the morphology of synthesized product⁹⁻¹⁰. As previously stated, the type of alkali strongly influences the gel formation and affect the transformation to crystalline aluminosilicate. In this manuscript we report the results of our studies using lithium hydroxide as the hydrolytic agent to synthesize Li-zeolites and study the effect of lithium hydroxide ratio on type and morphology of the products.

7.3 Experimental

7.3.1 Materials

Fumed silica (SiO₂, surface area 473.5 m²/g, average particle size of 0.007 μm) and aluminum hydroxide hydrate (Al(OH)₃, surface area 50.77 m²/g), were purchased from Sigma Chemical Co. and used as received. Triethanolamine (TEA, N(CH₂CH₂OH)₃), and triisopropanolamine (TIS, N(CH₂CH(CH₃)OH)₃) were supplied by Carlo Erba Reagenti and Fluka Chemical AG., respectively, and used as received. Ethylene glycol (EG, HOCH₂CH₂OH) was obtained from J.T. Baker Inc. and distilled using fractional distillation prior to use. Lithium hydroxide (LiOH) was ordered from Fisher Chemicals and was used as received. Acetonitrile (CH₃CN) was obtained from Lab-Scan Co., Ltd. and distilled using standard purification methods prior to use.

7.3.2 Characterization

Fourier transform infrared (FTIR) spectroscopic analysis was conducted using a Bruker Instruments (EQUINOX55) spectrometer with a resolution of 4 cm⁻¹ to measure the absorbance by the functional groups. The solid samples were prepared by mixing 1% of sample with dried KBr, while the liquid samples were analyzed using Zn-Se window cell. In measuring molar mass of precursors, mass spectra were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system, using the positive fast atomic bombardment (FAB⁺-MS) mode and glycerol as a matrix. CsI was used as a reference, while a cesium gun was used as an initiator. The mass range used was from m/e = 20 to

3,000. Thermal properties and stability were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was performed using a Perkin Elmer TGA7 analyzer while DSC was conducted with a Netzsch instrument: DSC200 Cell and TASC 414/3 controller at a heating rate of 10°C/min under nitrogen atmosphere. Aluminum pans were used in the DSC analysis with sample sizes of 5 – 10 mg, while a platinum pan was used in the TGA with sample size of 10 – 20 mg. For liquid and gel samples a high-pressure gold cell was used with the sample size of 10-20 mg. Simultaneous Thermal Analyzer (STA) was also employed for measuring the thermal stability and phase transformation of synthesized zeolite at a heating rate of 20°C/min under nitrogen atmosphere. The testing was carried out with a Netzsch instrument: STA409 EP. The sample size for this measurement was in the range of 10 - 50 mg using an alumina-crucible as the sample cell. Crystallinity of products were characterized by Rigaku X-Ray Diffractometer at a scanning speed of 5 degrees/sec using CuK α . The working range was 5° – 50° theta/2 theta. SEM micrographs were obtained with a JEOL 5200-2AE scanning electron microscope. Electron Probe Microanalysis (EPMA) was used to analyze the sample in micro-scale for both qualitative and quantitative elemental analysis with the X-Ray mode detector (SEM/EDS; Energy Dispersive Spectroscopy) to obtain product compositions. Particle sizes and particle size distributions were determined using a Malvern Instruments Mastersize X Ver.2.15 analyzer. Water was used as a mobile phase. Hydrothermal treatment by microwave heating technique was conducted using a MSP1000, CME Corporation (Spec. 1,000W and 2,450 MHz) oven. Samples were heated in a Teflon-lined digestion vessel sealed with a Teflon cap using inorganic digestion mode with time-to-temperature program.

7.3.3 Precursor Synthesis

By following Oxide-One-Pot-Synthesis (OOPs) process, Silatrane was synthesized by mixing 0.10 mol silicon dioxide and 0.125 mol triethanolamine in a simple distillation set using 100 mL ethylene glycol as solvent¹¹. The reaction was carried out at the boiling point of ethylene glycol under nitrogen atmosphere set for 10 h to remove water as by-product and ethylene glycol from the system. Excess

ethylene glycol was removed under vacuum (10^{-2} torr) at 110°C . The brownish white solid was washed with dried acetonitrile for three times. Approximately 95% yield of white powder product was obtained and characterized using FTIR, TGA, DSC and FAB^+ -MS. The product was named as SiTEA.

Alumatrane synthesis was also followed the OOPs process, which the procedure is similar to silatrane synthesis. It was synthesized from 0.1 mol aluminum hydroxide and 0.125 mol triisopropanolamine¹². The crude product was washed with dried acetonitrile for three times which $\sim 90\%$ yield product was obtained and characterized using FTIR, TGA, DSC and FAB^+ -MS. The product was named as ALTIS.\

7.3.4 Sol-Gel Process and Microwave Technique

SiTEA and ALTIS were mixed with lithium hydroxide solution at room temperature at a ratio of $\text{SiO}_2:\text{xAl}_2\text{O}_3:\text{yLi}_2\text{O}:\text{zH}_2\text{O}$ (where $0.0115 < x < 6$, $0 \leq y \leq 10$ and $63 \leq z \leq 1000$). The solution mixture was aged for at least 24 h to obtain full gel formation and then transferred into a Teflon vessel, sealed with Teflon cap, for further hydrothermal treatment using microwave heating technique. The solution mixtures containing different ratios of $\text{SiO}_2:\text{xAl}_2\text{O}_3:\text{yLi}_2\text{O}:\text{zH}_2\text{O}$ were treated for various times and temperatures and then the resulting white powder products were washed three times using distilled water. The products were finally dried at 75°C for 15 h. The synthesized products didn't have any carbon component in the pores or the framework as confirmed by EDS/SEM and STA.

7.4 **Results and Discussion**

Gels started to form at the $\text{SiO}_2:\text{Li}_2\text{O}$ of 1:0.01 and the $\text{SiO}_2:\text{H}_2\text{O}$ ratio had to be at least 1:63 to obtain a better heat transfer and homogeneous dispersion of particle in solution. However, a better condition for microwave heating technique was at $\text{SiO}_2:\text{H}_2\text{O}$ ratios of 1:410. $\text{SiO}_2:\text{Li}_2\text{O}$ ratios were varying from 1:0.7 to 1:10. When with at $\text{SiO}:\text{Li}_2\text{O}$ ratio was grater than 1:4, base on XRD's result, only Silicon Nitride was obtained after passing hydrothermal treatment. The gel formation

started from a cloudy solution caused by low dissolution of atranes due to the weak base of LiOH. Thus the aging time of the mixture had to be at least 24 h.

7.4.1 Gel Transformation to Aluminosilicate and Effect of Microwave heating temperature

Gel transformation to aluminosilicate was studied using high pressure DSC cell at a heating rate of 10 °C/min as illustrated in figure 1. The gel transformation started at 103.6 °C and the maximum transformation rate was at 107 °C. The transformation was endothermic, consuming 21.205 J/g. However, treating the same gel under hydrothermal conditions by using microwave-heating technique, the fully crystalline aluminosilicate started to form at 70 °C as observed in figure 2. These differences are most likely due to the specific interaction between the microwave radiation and the polar functional groups of the precursors, resulting in a faster, simpler, cleaner and very energy efficient synthesis¹. Moreover, at different microwave heating temperatures, different types of products were obtained as shown in figure 2. By XRD matching showed that at low temperature (in range of 70 – 90 °C), the EDI type zeolite (PDF#30-0742, $\text{Li} \cdot \text{Al} \cdot \text{SiO}_4 \cdot \text{H}_2\text{O}$, $16.6 \text{T}/\text{\AA}^3$) was obtained while at high temperature (greater than 90 °C), the ABW product (PDF#41-0554, $\text{Li}_4\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 4\text{H}_2\text{O}$, $19 \text{T}/\text{\AA}^3$) was produced. The higher the temperature, the higher packing density, due to the collapse of the zeolite networks at high temperature. The unit cell structure and crystal morphology of EDI product were in cubic form as found in figure 3(a), while those of ABW were needle like since the growth in y-direction was lesser than that in x-z direction (figure 3(b)). The Si:Al ratio of synthesized product was at 1.20:1 for EDI and 1.33:1 for ABW. The Si:Al ratio of both products was higher than the information obtained from the XRD library (Si:Al = 1:1 for both). EDI was thermally stable up to ~270 °C at this temperature it changed to an amorphous solid first and then transformed to Lithium Aluminum Silicate (PDF#26-0839, LiAlSiO_4) at 400 °C, as illustrated in figure 4(a). While ABW was thermally stable up to ~300 °C after which it changed to Lithium Aluminum Silicate, $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$ (PDF#40-0063) first and then to LiAlSiO_4 (PDF#26-0839) form at 640 °C (figure 4(b)). ABW had higher thermal stability than EDI due to the higher Si-content¹³.

Based on the SEM result (figure 5), the nicest looking crystals were obtained at 90 °C for EDI and at 110 °C for ABW. At temperature higher than 110 °C, ABW crystals were smaller and more irregular (figure 5(d)) most likely due to high rate of nucleation versus growth of existing crystals. The Si:Al ratios of the synthesized products increased in the range of 1 – 1.5 with increasing microwave heating temperature. At ~50 °C, the Si:Al ratio was approximately one which closely matched with the literature XRD data.

7.4.2 Effect of Si:Al ratio in the precursors:

After fixing the feed ratios at $\text{SiO}_2:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and microwave heating temperature at 110 °C/300 min, the Si/Al ratio was varied from 0.167 to 87. Changing Si:Al loading ratio led to the formation of different types of products as shown in figure 6. At Si/Al loading ratios of more than 1, only lithium silicate (PDF#29-0829, Li_2SiO_3) was found. For Si/Al loading ratio of 1, only ABW product was produced and for Si/Al loading ratio of 0.25 – 0.5, only EDI product was obtained. At Si/Al loading ratio of 0.2, a mixture of ABW and aluminum hydroxide were produced while at Si/Al loading ratios less than 0.167, only aluminum hydroxide product was obtained. The morphologies of the synthesized products changed with the changing the Si/Al loading ratio, even though in some cases the XRD results were the same (figure 7). The higher the Al compound loading, the more irregular crystals were produced due to the hexagonal-coordination favored by Al^{13} . The Si/Al ratio of synthesized product increased with the Si/Al loading ratio.

7.4.3 Effect of Li_2O Concentration

The effect of Li_2O concentration was studied after fixing the loading ratios of the other components at: $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:410\text{H}_2\text{O}$ with the synthesis temperature and time fixed at 110 °C and 300 min. The $\text{Li}_2\text{O}/\text{SiO}_2$ ratio was varied from 0.7 to 5. Surprisingly at $\text{Li}_2\text{O}/\text{SiO}_2$ ratio of 1, the FAU type zeolite (PDF#39-1380, $\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$, $12.7 \text{ T}/\text{\AA}^3$) was obtained mixed with LZ-200 (PDF#47-0716, $\text{Li}_{2.12}\text{Al}_2\text{Si}_2\text{O}_{8.06}$). The XRD spectra of the products are given in figure 8 and the crystal morphology and unit cell structure of FAU is illustrated in figure 9. The

Si:Al ratio of synthesized product was $\sim 1.70:1$ which was lower than the FAU and higher than LZ-200 data obtained from XRD library (Si:Al = 2 for FAU and 1:1 for LZ-200). Based on the average Si/Al ratio and crystal morphology, the major product was FAU type zeolite. The product was thermally stable until ~ 650 °C as observed by STA and XRD (figure 10). Upon further heating the product became amorphous first and then transformed to lithium aluminosilicate (LiAlSiO_4) at 1000 °C. At $\text{Li}_2\text{O}/\text{SiO}_2$ ratio of 2, the mixture of EDI and FAU were found. For $\text{Li}_2\text{O}/\text{SiO}_2$ ratio equal to 3, only the ABW type was found. At $\text{Li}_2\text{O}/\text{SiO}_2$ ratio of 4, a mixture of EDI and silicon nitride (PDF#33-1160, Si_3N_4) were produced and at $\text{Li}_2\text{O}/\text{SiO}_2$ more than 4, only silicon nitride was obtained. Moreover, the morphologies of synthesized products were different. The XRD spectra of the products at $\text{Li}_2\text{O}/\text{SiO}_2$ ratios of 2 and 3 indicated the major product was EDI, the morphology of those conditions was not the same, which at higher Al-content, more irregular product was obtained as illustrated by SEM (figure 11). These figure shows that the Li_2O concentration was had a strong influence on the product type due to the changing of hydroxyl concentration, which affected the rate of dissolution of aluminosilicate gel in the crystallization step. The Si/Al ratio of synthesized product was changed via the changing of product types.

7.4.4 Effect of Microwave Heating Time

By fixing the precursor ratios at $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and the temperature 110 °C, we studied the effect of microwave heating time. Figure 12 shows that the morphologies of synthesized products were changed with heating time. A mixture of EDI and ABW type morphologies were mostly observed except at 60 and 300 min when pure EDI and ABW were found respectively. Most products tended to form in EDI structure type only at 300 min, pure ABW was found. ABW structure is unstable resulting from higher packing density and higher ring strain as illustrated in the unit cell structure (figure 3). However the possibility in having both structures might come from the small radius of Li ion, which can move and diffuse very easily and had very low transformation energy to aluminosilicate as observed by DSC. Moreover, the secondary building unit of EDI and ABW are mostly the same. By lowering the microwave heating temperature to

90 °C, only EDI product was found and the fully crystalline product was obtained at 60 min. Based on SEM's results (figure 13), most particles have size in range of ~1 to 1.5 μm . However, there also have some small particles (~0.5 μm) indicating the formation of new nuclei right after some product sediment. Even when the reaction time was set for 10 h at 90 °C, only EDI product was formed. These findings confirm that in synthesizing zeolites, higher energy supplied by microwave heating caused changes in morphology and structure type. In changing the $\text{Li}_2\text{O}/\text{Si}_2\text{O}$ ratio from 3 to 1, with increasing aging and synthesis time only FAU type zeolite was produced with the fully crystalline product forming at 120 min (figure 14).

7.5 Conclusions

Lithium aluminosilicates can be one step synthesized directly from alumatrane and silatane by the sol-gel process and microwave heating technique using lithium hydroxide as hydrolytic agent. By using microwaves as the energy source for hydrothermal treatment, transformation temperatures to aluminosilicate lower than that seen in the DSC are obtained due to the exact nature of between the microwave radiation and the functional groups of molecules. This results in a faster, simpler, higher purity and very energy efficient method. Moreover, the radius of Li^+ -ion was small (compared to K^+ and Na^+ ion) resulting in lower steric hindrance in aluminosilicate formation. By fixing the Si/Al ratio at 1, $\text{Li}_2\text{O}/\text{SiO}_2$ at 3 and microwave heating time of 300 min, two structure types were produced at different temperatures. High temperature provided a higher packing density product (ABW) due to the collapse of framework. The Si/Al ratio of the synthesized product increased as increasing temperature. Both EDI and ABW were not thermally stable. They changed to lithium aluminate silicate (denser materials) at temperatures higher than 500 °C, because the unit cell structure of both products is mostly composed of high ring strain (T4-rings). Changing the Si/Al loading ratio strongly influenced the morphologies and/or the type of synthesized products. Higher Al-content led to higher amounts of irregular products, due to favoring of octahedral structure by the Al atom/ion. $\text{Li}_2\text{O}/\text{SiO}_2$ starting ratio strongly affected the types structures obtained in the products. With increasing $\text{Li}_2\text{O}/\text{SiO}_2$ ratio, the structure type changed to

higher packing density product. Lowering the $\text{Li}_2\text{O}/\text{SiO}_2$ ratio to 1, FAU type zeolite was produced. Fixing the precursor ratios at $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and microwave heating temperature at $110\text{ }^\circ\text{C}$, a mixture of EDI and ABW was observed most of the time due to the low energy requirement of aluminosilicate transformation. Moreover, Li ion radius was small causing less steric effect in aluminosilicate formation. Lowering the microwave heating temperature to $90\text{ }^\circ\text{C}$, only EDI product having lower packing density than ABW was produced confirming that at $110\text{ }^\circ\text{C}$, the energy provided was too high.

7.6 Acknowledgement

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7.7 References

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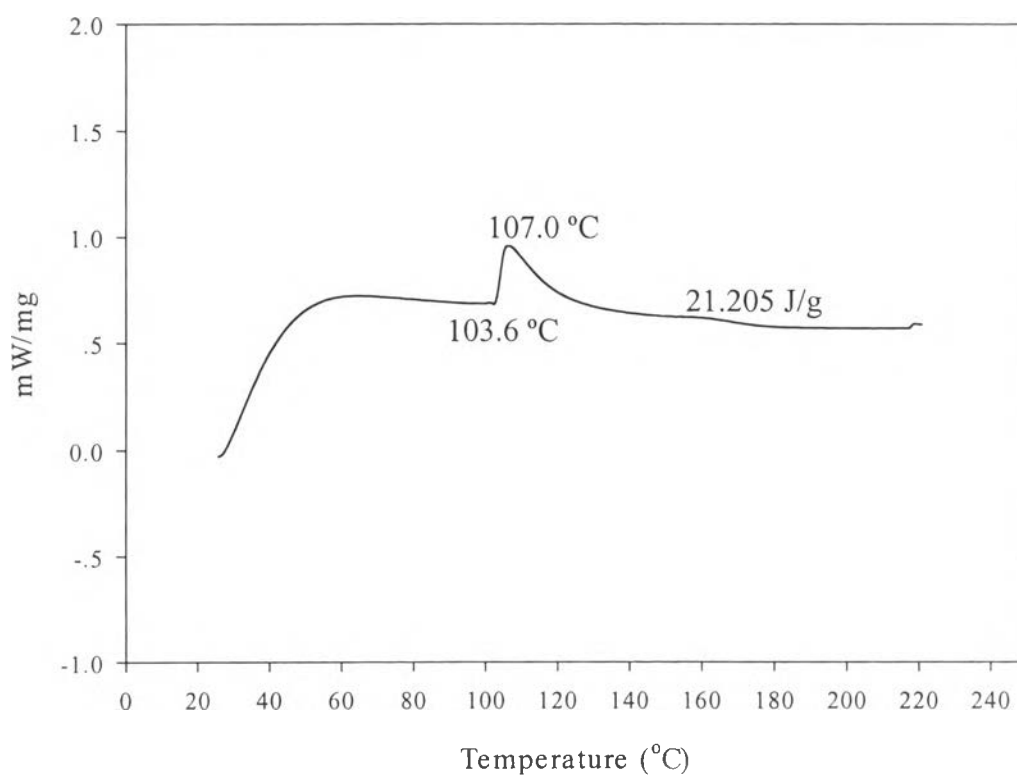


Figure 7.1 DSC trace of gel transformation to aluminosilicate using a high pressure DSC cell at a heating rate of 10 °C/min and gel composition of 1SiO₂:0.5Al₂O₃:0.7Li₂O:410H₂O

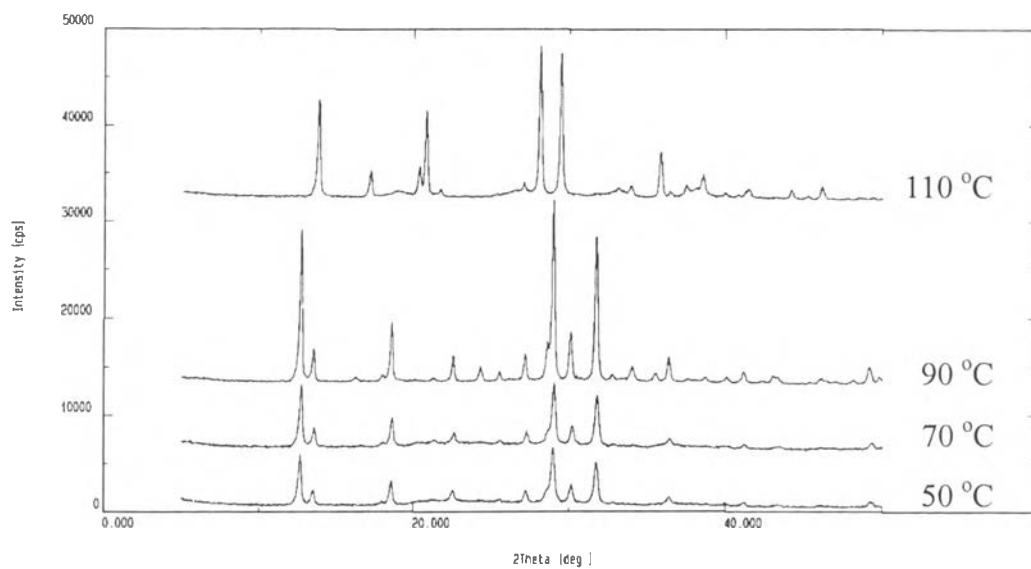
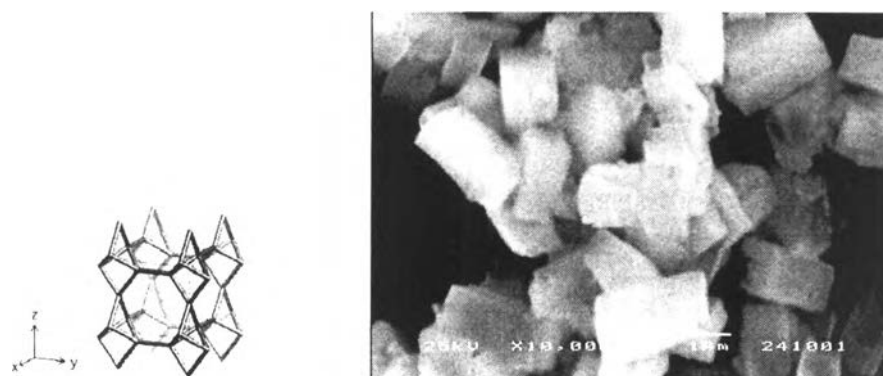
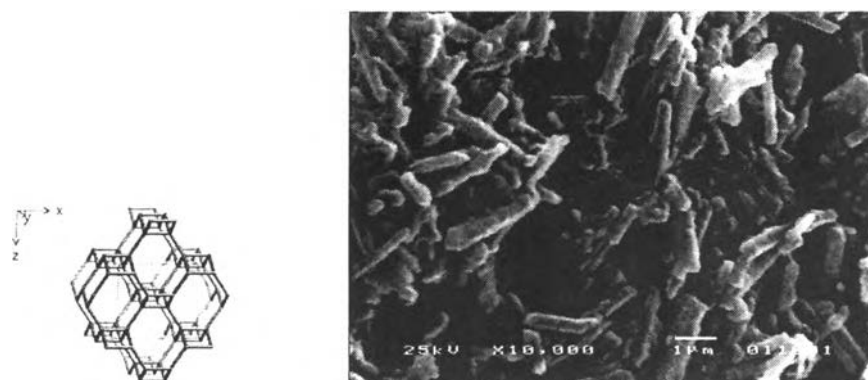


Figure 7.2 Effect of microwave heating temperature on aluminosilicate crystallinity synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:41\text{H}_2\text{O}$ and $X\text{ }^\circ\text{C}/300\text{ min}$



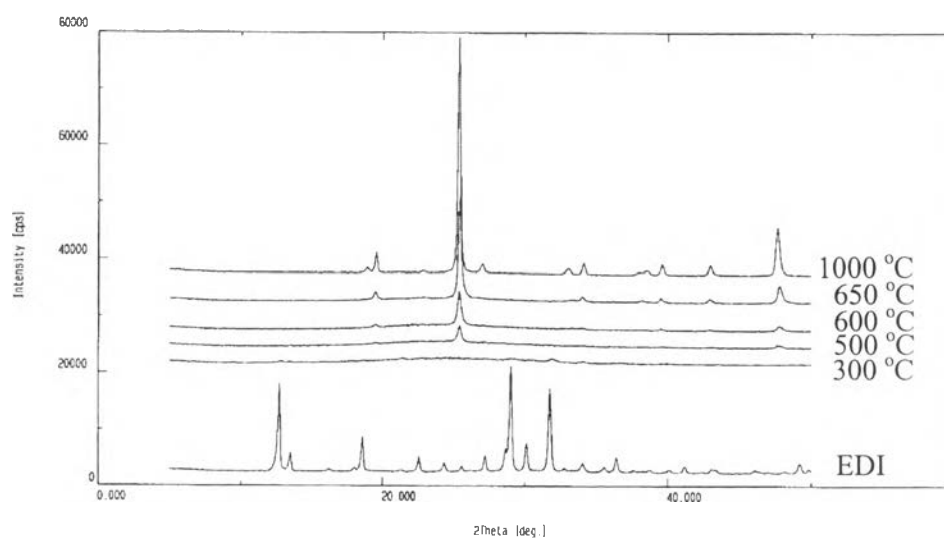


(a)

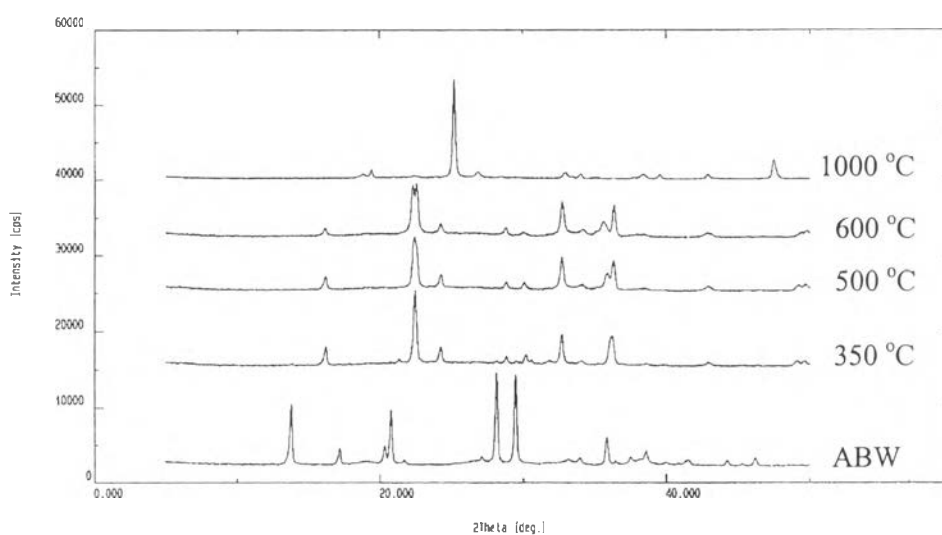


(b)

Figure 7.3 Unit cell structures and crystal morphologies of (a) EDI and (b) ABW product



(a)



(b)

Figure 7.4 XRD spectra of EDI (a) and ABW (b) products synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and 90 °C/300 min as a function of temperature.

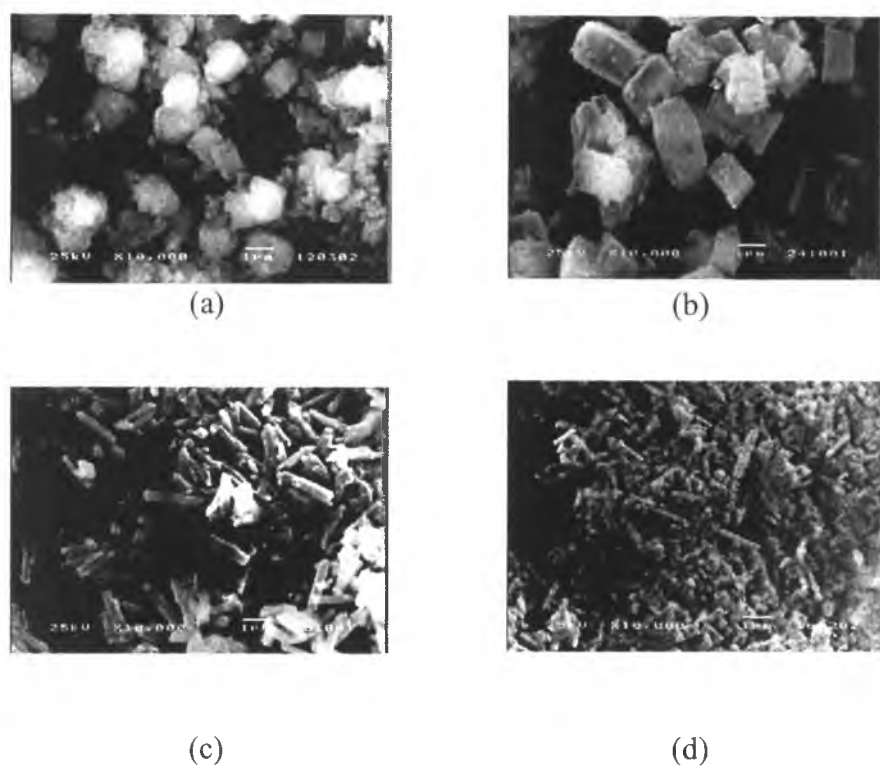


Figure 7.5 Crystal morphology of aluminosilicate synthesized from 1SiO₂:0.5Al₂O₃:3Li₂O:410H₂O and X °C/300 min; (a) 70, (b) 90, (c) 110, (d) 150 °C

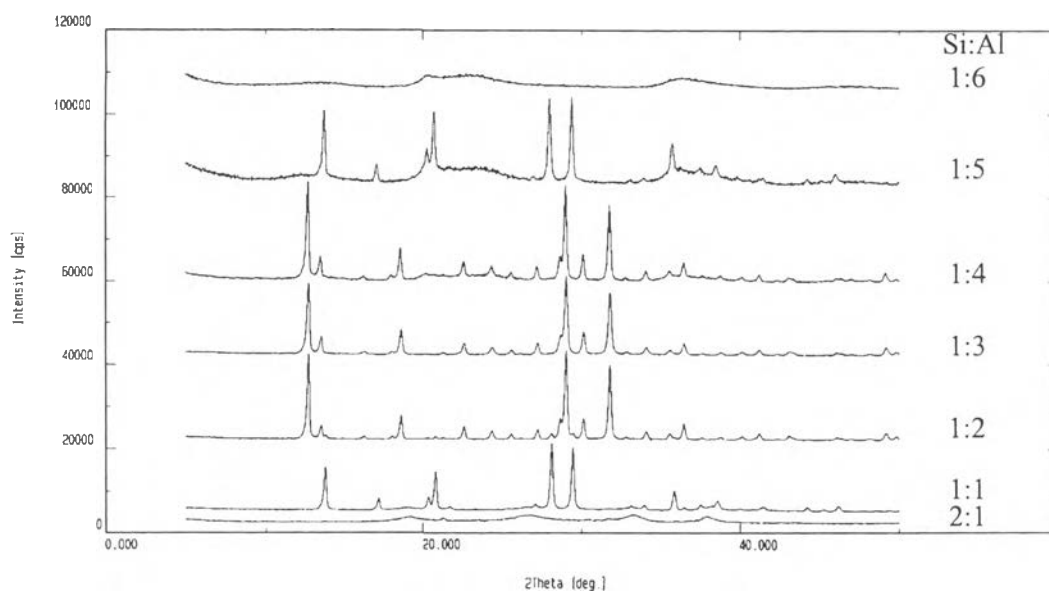


Figure 7.6 Effect of starting Si/Al ratio on aluminosilicate synthesized from $1\text{SiO}_2:X\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ ($X = 0.25 - 3$) and $110^\circ\text{C}/300\text{ min}$

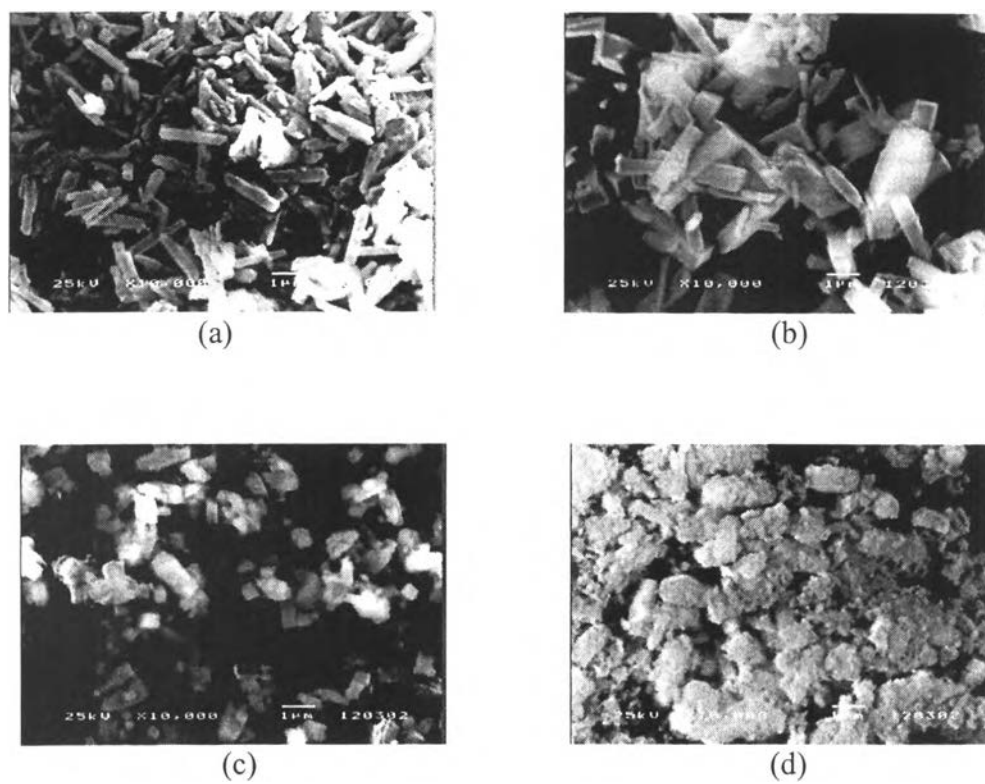


Figure 7.7 Crystal morphology of aluminosilicate synthesized from $1\text{SiO}_2:X\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ ($X = 0.25 - 3$) and $110^\circ\text{C}/300\text{ min}$; Si:Al = (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4 respectively

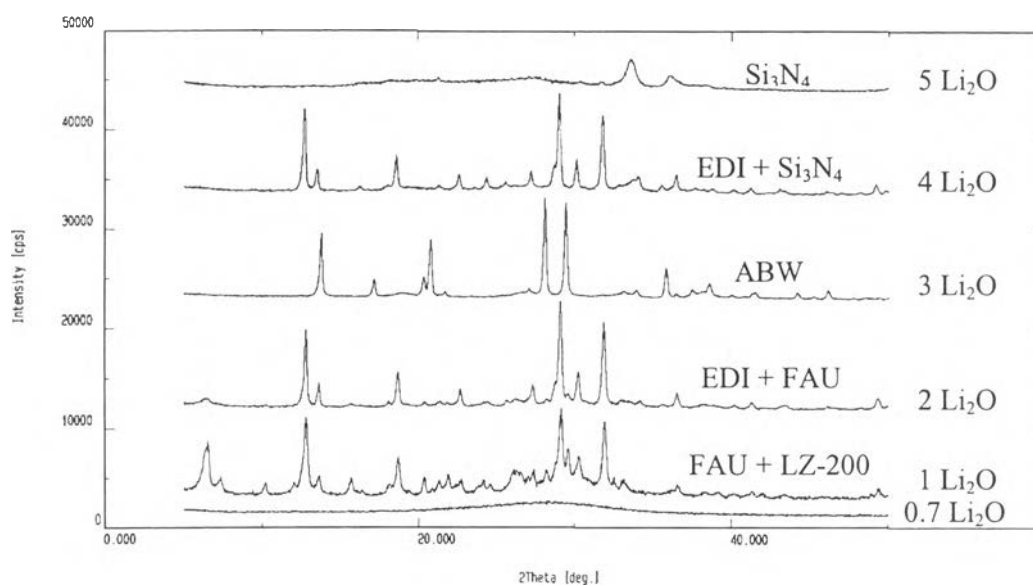


Figure 7.8 Effect of Li_2O concentration on morphology of aluminosilicate synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3: X \text{Li}_2\text{O}:410\text{H}_2\text{O}$ ($X = 0.7 - 5$) and $110^\circ\text{C}/300$ min

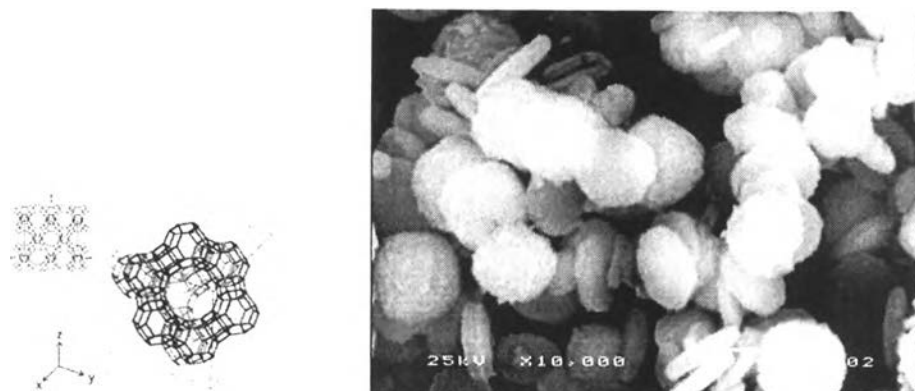


Figure 7.9 The unit cell structure, crystal morphology and Si/Al ratio of FAU synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:1\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and $110\text{ }^\circ\text{C}/300\text{ min}$

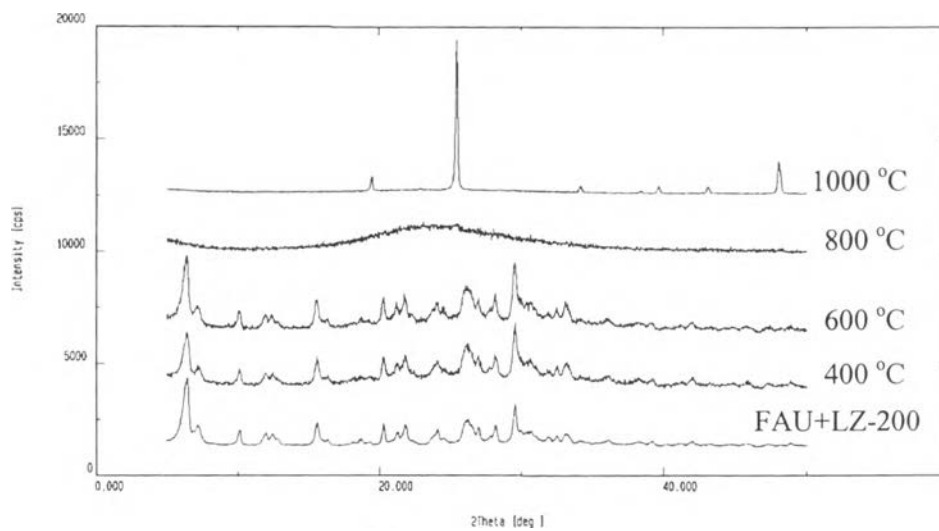


Figure 7.10 XRD spectra as function of temperature for the FAU product synthesized from $1\text{SiO}_2: 0.5\text{Al}_2\text{O}_3: 1\text{Li}_2\text{O}: 410\text{H}_2\text{O}$ and $110\text{ }^\circ\text{C}/300\text{ min}$

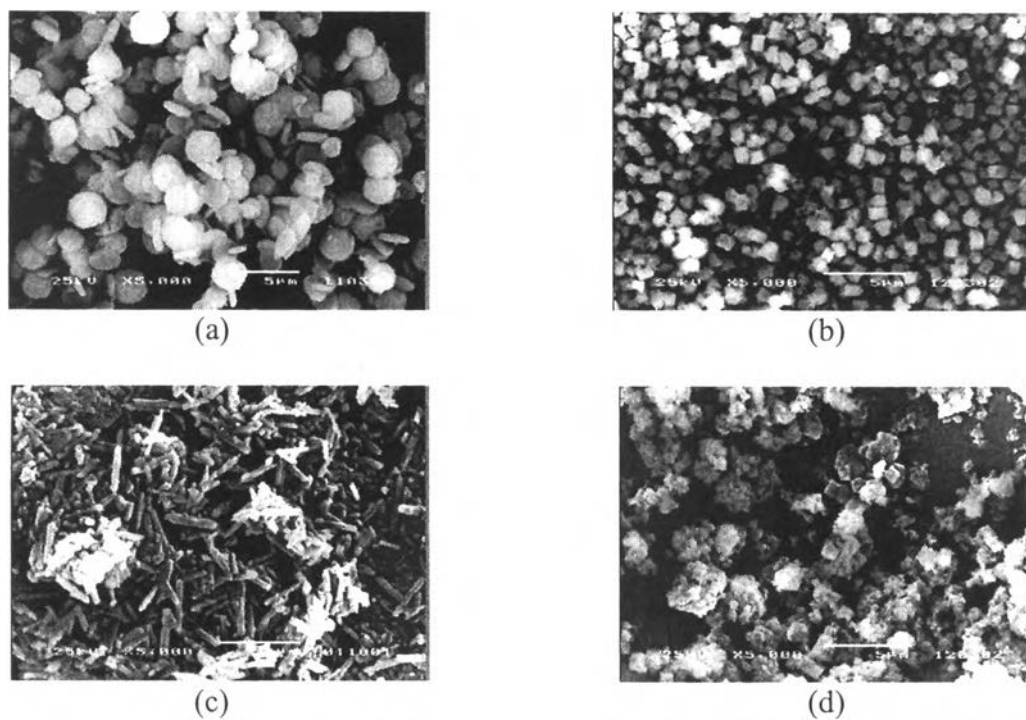


Figure 7.11 Crystal morphology of aluminosilicate synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:X\text{Li}_2\text{O}:410\text{H}_2\text{O}$ ($X = 0.7 - 5$) and $110\text{ }^\circ\text{C}/300\text{ min}$

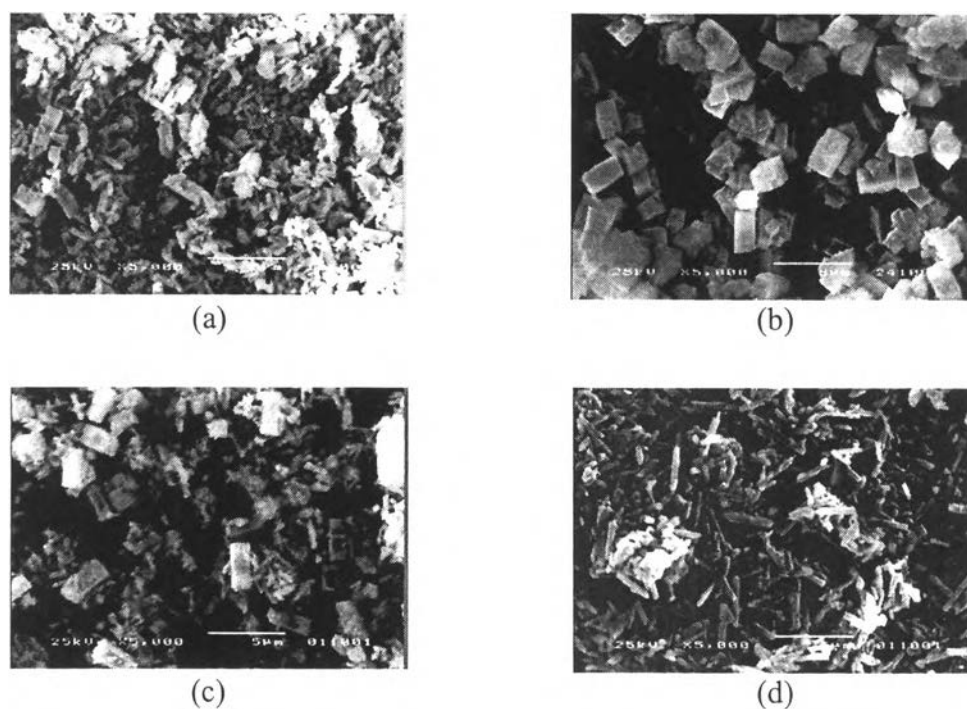


Figure 7.12 Transformation to aluminosilicate as a function of time, starting with $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and $110^\circ\text{C}/X$ min; (a) 40, (b) 60, (c) 120 and (d) 300 min

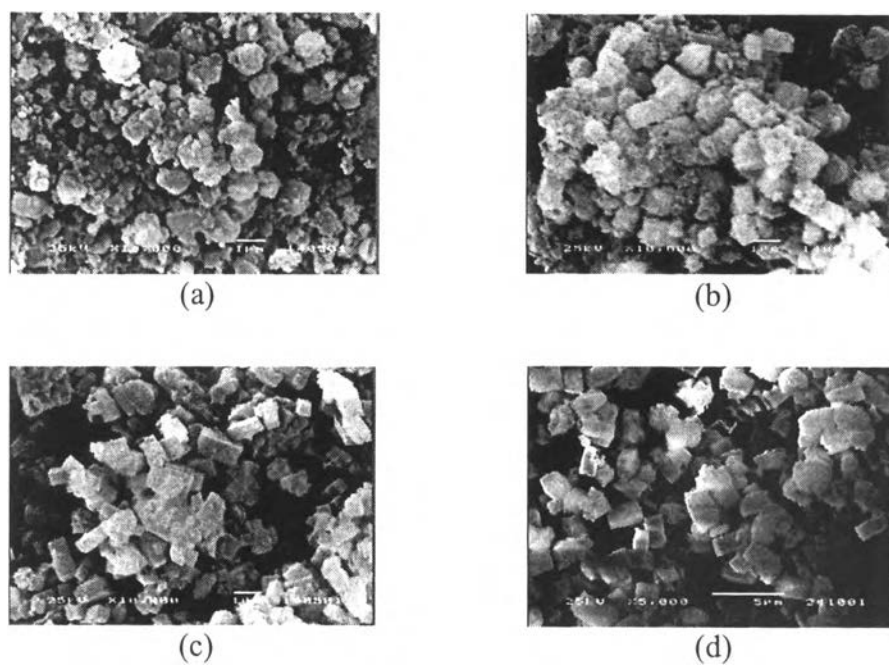


Figure 7.13 Transformation to aluminosilicate synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and $90^\circ\text{C}/X$ min; (a) 20, (b) 40, (c) 60 and (d) 120 min

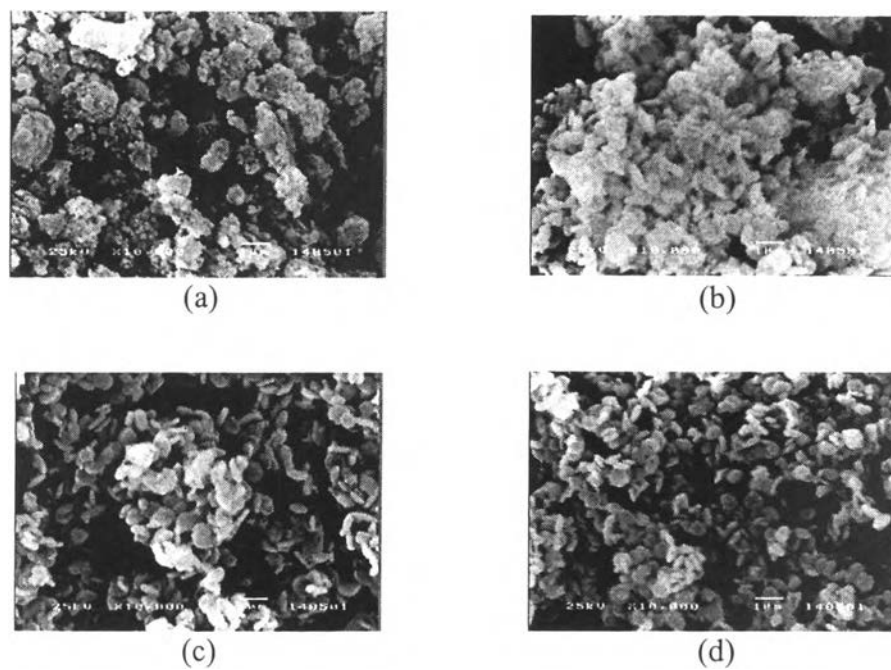


Figure 7.14 Transformation to aluminosilicate synthesized from $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:1\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and $110^\circ\text{C}/X$ min; (a) 80, (b) 100, (c) 120 and (d) 180 min