

**CHAPTER VI**  
**MICROWAVE PREPARATION OF K-ZEOLITE DIRECTLY FROM**  
**ALUMATRANE AND SILATRANE**

*(Chemistry of Materials, Submitted)*

**6.1 Abstract**

K-zeolite can be one-step synthesized by sol-gel process and microwave heating technique using alumatrane and silatrane as precursors and potassium hydroxide as hydrolytic agent. By fixing the component ratios at  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and microwave heating temperature at 150 °C for 240 min, XRD's results indicated that the synthesized product was closely matched with zeolite K-H, an unknown structure type, which was named as PPC-ZM-1. The morphology of synthesized product was like flower petals and the Si:Al:K ratio of synthesized product was 1.98:1:0.82. Varying Si:Al loading ratio highly effected the crystal morphology but the microwave heating time of all conditions in producing crystalline aluminosilicate was the same. Increasing microwave heating temperature or varying the  $\text{K}_2\text{O}:\text{SiO}_2$  ratio also influenced the crystal morphology of the synthesized product. Moreover varying the  $\text{K}_2\text{O}:\text{SiO}_2$  ratio also affected on the microwave heating time. Further heating after obtaining crystalline product contributed to the changing of crystal morphology to smaller and more agglomerated particles.

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

## 6.2 Introduction

Zeolites are well-defined microporous crystalline material and have been investigated extensively and applied as solid catalysts in the field of petrochemical industries due to their several advantages compared to homogeneous catalyst, e.g. ease of recovery, enhanced selectivity and stability and recycling of the catalyst<sup>1</sup>. They have crystallographically ordered and well-defined pores and cages of molecular dimension in which water molecules and charge compensation cations are situated. The structure, shape and chemical composition of pores and cages are important, for instance catalytic reactions taking place on the inner surface of zeolite K-L show that it is a highly active and selective catalyst for chlorination of aromatics<sup>2</sup> while zeolite K-Y encapsulating Ru(II) complex can be used with visible light-induced electron transfer reactions<sup>3</sup>. Alkali cations are also one of key parameters in selecting type of catalyst, which affects pore opening size and chemistry such as Na-load zeolite LTA is used for gas separation based on permeability of materials<sup>4-5</sup>. While for K-doped K-LTA zeolite, additional potassium atoms per  $\alpha$ -cages was found to show ferromagnet (FM)-like transition property, causing from the 4s-electrons of the guest K-atoms delocalized as 1s and 1p electrons of quantum states formed in the  $\alpha$ -cages<sup>6</sup>.

Zeolite synthesis is conventionally performed by hydrothermal crystallization under alkaline condition with use of an amorphous aluminosilicate gel as the starting material<sup>7-11</sup> or hydrothermal conversion in alkali or neutral solution<sup>12</sup>. Combining hydrothermal crystallization with microwave heating technique has been aggressively developed due its advantages of very short time, broad composition range, small zeolite particle size, narrow zeolite particle size distribution and high purity<sup>13-16</sup>. Most synthetic zeolites are prepared in the presence of Na<sup>+</sup> cation. In making other cation-loaded zeolites, the conventional ion-exchange method is employed<sup>2-3</sup> because of its ease. Moreover, some cations especially K<sup>+</sup> is known to retard the crystallization rate<sup>17</sup> and hinder the aggregation of amorphous gel by forming a double layer around the silica particle<sup>18</sup>. As a result

only a few publications report on the in situ synthesis with the  $K^+$  cation, e.g. synthesis of SUZ-4 in the  $K^+/TEA^+$  system<sup>19</sup>.

According to our previous results, silatrane or silatrane mixed with alumatrane can be used as starting material for the sol-gel process<sup>20-21</sup>. They have the trialkoxyamine ligand that is able to coordinate with the metal atom to form inorganic-organic micelles and to give moderately inert complexes in aqueous or basic solutions<sup>22-23</sup>. By using sodium hydroxide as hydrolytic agent and treating the amorphous gel under hydrothermal condition, crystalline aluminosilicates or zeolites were obtained. ANA and GIS were found at the same loading composition but at different temperatures<sup>21</sup>, while LTA were produced at different loading composition<sup>24</sup>. In this project we report the results of our studies using potassium hydroxide as the hydrolytic agent for the sol-gel process and treating the gel by hydrothermal for making crystalline aluminosilicate.

## 6.3 Experimental

### 6.3.1 Materials

Fumed silica ( $SiO_2$ , surface area  $473.5\text{ m}^2/\text{g}$ , average particle size of  $0.007\text{ }\mu\text{m}$ ) and aluminum hydroxide hydrate ( $Al(OH)_3$ , surface area  $50.77\text{ m}^2/\text{g}$ ), were purchased from Sigma Chemical Co. and used as received. Triethanolamine (TEA,  $N(CH_2CH_2OH)_3$ ), and triisopropanolamine (TIS,  $N(CH_2CHCH_3OH)_3$ ) were supplied by Carlo Erba Reagenti and Fluka Chemical AG., respectively, and used as received. Ethylene glycol (EG,  $HOCH_2CH_2OH$ ) was obtained from J.T. Baker Inc. and distilled using fractional distillation prior to use. Potassium hydroxide (KOH) was ordered from Carlo Erba Reagenti and was used as received. Acetonitrile ( $CH_3CN$ ) was obtained from Lab-Scan Co., Ltd. and distilled using standard purification methods prior to use.

### 6.3.2 Instrumentals

Fourier transform infrared (FTIR) spectroscopic analysis was conducted using a Bruker Instruments (EQUINOX55) spectrometer with a resolution of  $4\text{ cm}^{-1}$  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<sup>+</sup>-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) mode. 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 a Rigaku X-Ray Diffractometer at a scanning speed of 5 degrees/sec using CuK $\alpha$  as a source and CuK $\beta$  as a filter. 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.

### 6.3.3 Precursor Synthesis

By using Oxide One Pot Synthesis process (OOPS), 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 solvent<sup>20,25</sup>. The reaction was carried out at the boiling point of ethylene glycol under nitrogen atmosphere 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. The product was named as SiTEA.

Alumatrane was also synthesized by OOPS process using a 0.1 mol aluminum hydroxide and 0.125 mol triisopropanolamine<sup>26</sup>. The crude product was washed three times with dried acetonitrile with ~90% yield. The product was named as AlTIS.

### 6.3.4 Sol-Gel Process and Microwave Technique

Potassium aluminosilicate gels were prepared by the sol-gel process using SiTEA and AlTIS as precursors and potassium hydroxide as the hydrolytic agent. Gel formation was studied at various ratios:  $\text{SiO}_2 : x\text{Al}_2\text{O}_3 : y\text{K}_2\text{O} : z\text{H}_2\text{O}$  ( $0.010 \leq x \leq 2$ ,  $0 \leq y \leq 6$  and  $68 \leq z \leq 1000$ ). At high Si/Al ratio ( $\geq 10$ ), clear solutions were obtained due to the strongly basic potassium hydroxide enhancing the solubility of metal oxide network during the crystallization process and good complex formation of potassium ion with atrane<sup>23,27</sup>. The ratio of  $\text{H}_2\text{O}:\text{SiO}_2$  had to be more than 68 in order to get good dispersion. The solution mixtures were aged for 8 h before transferring to the Teflon lined vessel, sealed with a Teflon cap, for hydrothermal treatment in order to make the zeolite. They were heated at various temperatures and for varying times. The white precipitated products were washed with distilled water for three times. The products were characterized by SEM/EDS, XRD and TGA, DSC etc. The SEM/EDS results indicated that there was no carbon component left in the synthesized product.

## 6.4 Results and Discussion

Potassium hydroxide is the hydrolytic agent used in this project. The first difference observed when compared to using sodium hydroxide as the hydrolytic agent was that the reaction started from clear solutions. However, after the hydrothermal treatment, we could still obtain the white precipitated product.

### 6.4.1 Gel Transformation to Aluminosilicate and Effect of Microwave Heating Temperature

According to the DSC results shown in figure 1, gel transformation started to occur at 103.4°C and the maximum transformation was at 107.8 °C. The gel transformation was endothermic, the same as using sodium hydroxide as hydrolytic agent<sup>21</sup>. For reactant ratios fixed at  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$ , crystalline aluminosilicate product was obtained at microwave heating temperatures of 150 °C or higher, figure 2. This temperature is significantly higher than the DSC results. These might be that for DSC system using the temperature scan, solution might be transformed to semi-organized solid while treating in hydrothermal condition the gel was fully converted to fully crystalline. Thus it required higher temperature and a longer time. The XRD result of synthesized product closely matched that of zeolite K-H (PDF#16-0692,  $\text{K}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot x\text{H}_2\text{O}$ , Si:Al:Na = 2:1:1) which has the unknown structure type. The Si:Al:K ratio of synthesized product was found from SEM/EDS to be 1.98:1:0.82 (figure 3(a)). We named this zeolite PPC-ZM-1. The Si:Al ratio obtained from SEM/EDS was the same as the data received from XRD but the K/Al ratio was lower than that estimated from XRD. These might come from some aluminum atom still in the form of  $sp^1$ -hybridization causing the defected framework leading to very small needlelike structure showed by SEM. The needles appeared to aggregate into assemblies similar to flower petals, as shown in figure 3(b). The synthesized product was thermally stable up to ~600 °C, (figure 4). Above this temperature the product morphology slowly changed from crystalline to semi-crystalline.

Increasing microwave-heating temperature resulted in a denser structure (figure 5). At high temperatures, the number of bundle like structures

increased and smaller bundles were produced due to the higher rate of generation of new nuclei. Moreover, the higher the microwave heating temperature, the higher the pressure generated leading to coagulation of all the substrates promoting crystallization.

#### 6.4.2 Effect of Si:Al Ratio in Loading State

In this study, Si/Al loading ratio was varied from 0.5 to 100 at fixed SiO<sub>2</sub>:K<sub>2</sub>O:H<sub>2</sub>O ratios of 1:3:410. The microwave heating temperature as fixed 150 °C and microwave heating time was fixed at 300 min. The XRD spectra of the products obtained for all conditions were the same except at Si/Al ratios between 0.5-2. For Si/Al ratios of 0.5-1, the synthesized product was fully amorphous signs of crystallinity were seen with a Si/Al ratio of 2, (figure 6). However, the crystal morphologies changed with increasing Si/Al ratio (figure 7). As the ratio increased, smaller, denser and more agglomerated particles were obtained. Higher silica content might cause abundant of nuclei generation. Since more nuclei were generated, the irregularity in the structure of the synthesized product increased as illustrated in both figures 6 and 7. The Si:Al ratio of the synthesized product increased slightly with increasing Si:Al loading ratio.

#### 6.4.3 Effect of K<sub>2</sub>O Concentration

We varied the K<sub>2</sub>O:SiO<sub>2</sub> ratio from 1:1 to 6:1 while keeping constant all the other conditions (SiO<sub>2</sub>:0.1Al<sub>2</sub>O<sub>3</sub>:410H<sub>2</sub>O, T= 150°C, time = 300 min. XRD's results indicated that at the K<sub>2</sub>O/SiO<sub>2</sub> ratios above 2, only the PCC-ZM-1 was obtained (figure 8). Increasing K<sub>2</sub>O concentration did not change the XRD spectrum but affected on the crystal morphology of the synthesized product (figure 9) and microwave heating time (figure 10). The morphology changed from amorphous to semi-crystalline which has needle like structure and then changed to flower petals and bundle like respectively. At the K<sub>2</sub>O/SiO<sub>2</sub> ratio more than 4, the smaller and agglomerated bundles like crystallites were obtained. Surprisingly with increasing K<sub>2</sub>O/SiO<sub>2</sub> ratio, the microwave heating time dramatically dropped from 6 h at K<sub>2</sub>O/SiO<sub>2</sub> of 2 to 3 h at K<sub>2</sub>O/SiO<sub>2</sub> of 4 and then started increasing again for K<sub>2</sub>O/SiO<sub>2</sub> ratios higher than 4. It was found that for K<sub>2</sub>O/SiO<sub>2</sub> ratios higher than 4,

the particle sizes were much smaller and the reaction time was also increasing. The smaller particle size might be caused from a lot of nuclei generation at the same time due to fast dissolution of amorphous aluminosilicate gel at high metal hydroxide concentration<sup>18</sup>. Since the crystalline growth relies on the conventional colloid chemistry<sup>22</sup>, too many potassium ions at the surface of the micelle might cause the repulsive interactions between the organic-inorganic composite micelles in the system reducing the film drainage and retarding the crystalline formation. With increasing the  $K_2O/SiO_2$  ratio, the Si/Al ratio of synthesized product also decreased from 1.98 at  $K_2O/SiO_2$  of 3 to 1.77 at  $K_2O/SiO_2$  of 5, because of the higher pH values<sup>29</sup>.

#### 6.4.4 Effect of Microwave Heating Time

By fixing the reactant ratios at  $SiO_2:0.1Al_2O_3:3K_2O:410 H_2O$  (or Si/Al ratio of 5) and the temperature at 150 °C, the product changed from amorphous to completely crystalline after heating for 240 min (figure 11). Even after changing the Si/Al loading ratio from 5 to 100, fully crystalline product was obtained at the same time. Since both alumatrane and silatrane are dissolved completely in the potassium hydroxide solution, for all conditions, the solution mixtures were started from almost a clear solution before being subjected to hydrothermal treatment and good complex formation of atranes with potassium ion accelerated the dissolution of amorphous gel. The crystallization rate did not depend on the Si/Al loading ratio. The morphology study by SEM also indicated the same phenomena as observed by the XRD results as illustrated in figure 12. The morphology changed from amorphous to semi-crystalline at 180 min and fully crystalline at 240 min. The particle size increased first and then got smaller after heating for 360 min. The crystallites looked denser and more agglomerated. Many crystals appear to be fused together. These might be caused by the growing of new nuclei on the surface of the old crystals combined with dissolution and recrystallization of some crystals, since the system was heated under pressure for a long time. The Si/Al ratio of synthesized product was almost the same after passing 240 min or formation of fully crystals.



## 6.5 Conclusions

Potassium aluminosilicate was successfully synthesized by a one step sol-gel process using silatrane and alumatrane as precursors and potassium hydroxide as the hydrolytic agent. By fixing the reactant ratios at  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$ , the zeolite K-H named PPC-ZM-1 was synthesized by microwave heating at  $150^\circ\text{C}$  for 240 min, this temperature was higher by  $\sim 40^\circ\text{C}$  than that observed from the DSC trace. The morphology of the synthesized product was similar to flower-petals. Increasing the microwave heating temperature from  $150^\circ$  to  $170^\circ\text{C}$ , only PPC-ZM-1 was obtained with different crystal morphologies. Higher temperatures provided smaller particle size and bundle like products. At different Si/Al loading ratios, at  $\text{SiO}_2:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and microwave heating temperature of  $150^\circ\text{C}$  for 300 min, even when the Si/Al loading ratio was varied from 5 to 100, only PPC-ZM-1 was produced. As the loading ratio was changed, morphology changed to denser and smaller particles but the microwave heating time for each loading ratio was the same. With increasing  $\text{K}_2\text{O}/\text{SiO}_2$  ratios smaller particles and bundle like product morphology was obtained. Varying  $\text{K}_2\text{O}/\text{SiO}_2$  ratio also affected the microwave heating times, which dropped dramatically at first and then increased after reaching a minimum at a  $\text{K}_2\text{O}/\text{SiO}_2$  ratio of 4. With increasing microwave-heating time, the product particles tended to be smaller and more agglomerated.

## 6.6 Acknowledgement

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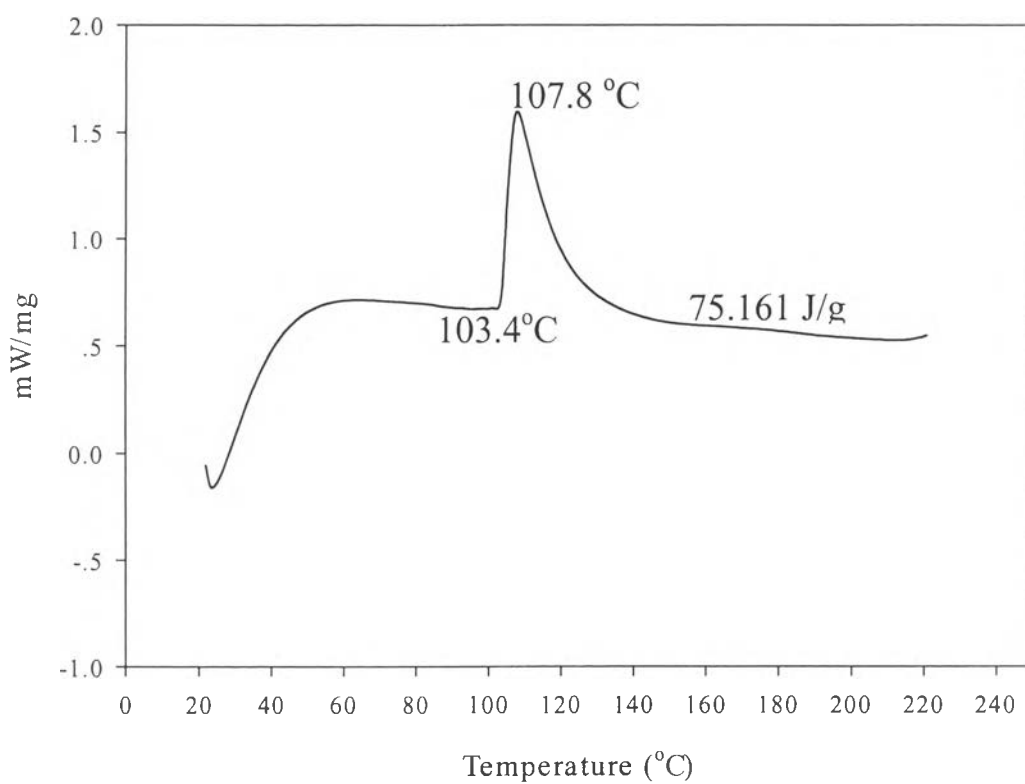
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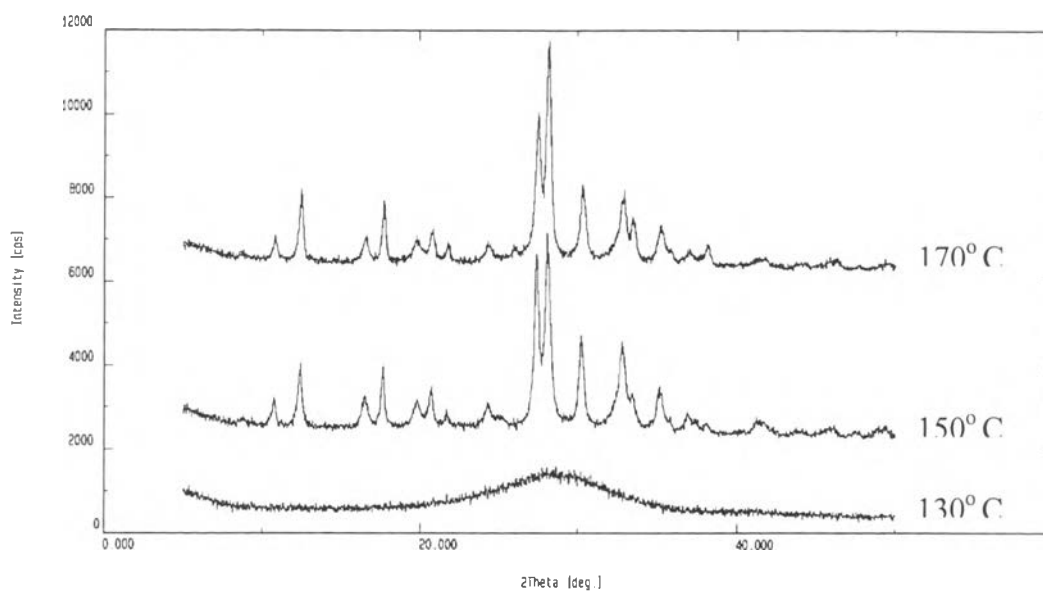
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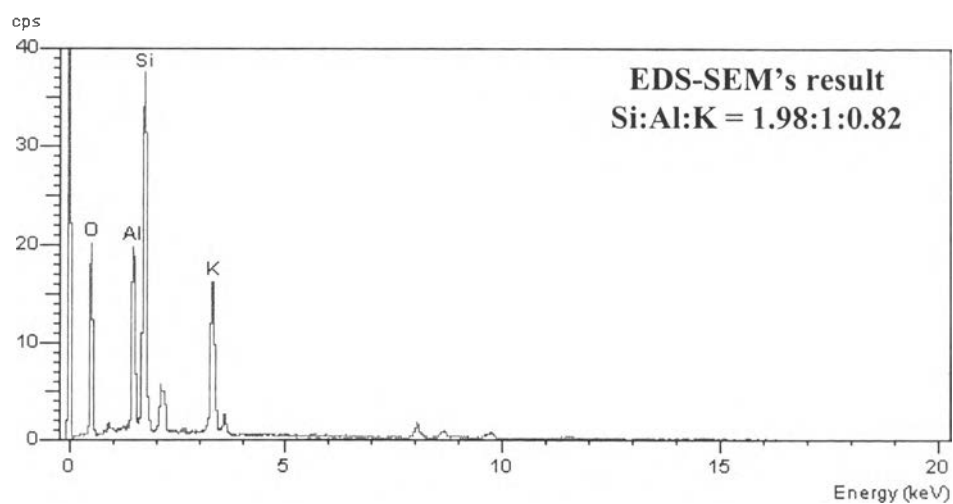
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**Figure 6.1** Thermal property of gel transformation to aluminosilicate using high presser DSC cell at heating rate of 10 °C/min and 1SiO<sub>2</sub>:0.1Al<sub>2</sub>O<sub>3</sub>: 0.7K<sub>2</sub>O:410H<sub>2</sub>O



**Figure 6.2** Effect of microwave heating temperature on K-aluminosilicate synthesized from 1SiO<sub>2</sub>:0.1Al<sub>2</sub>O<sub>3</sub>:3K<sub>2</sub>O:410H<sub>2</sub>O and X °C/300 min

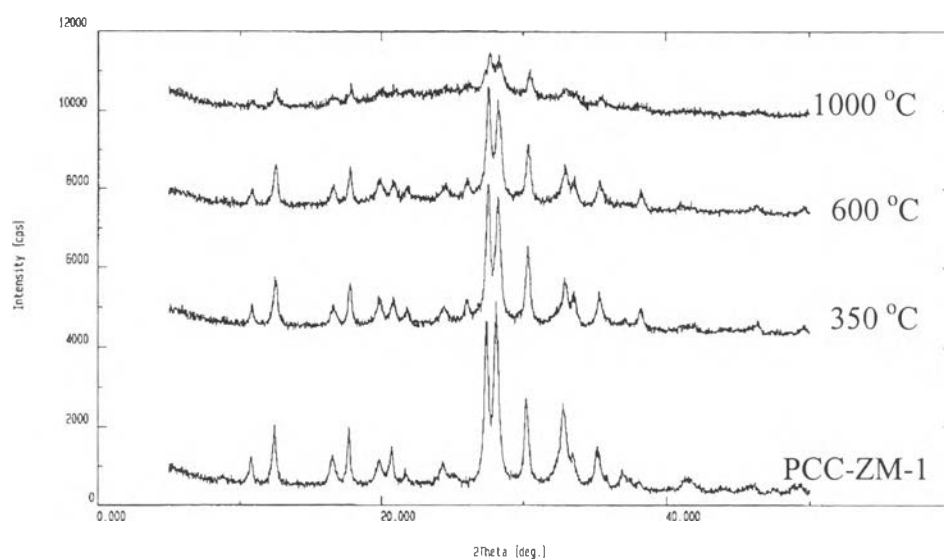


(a)



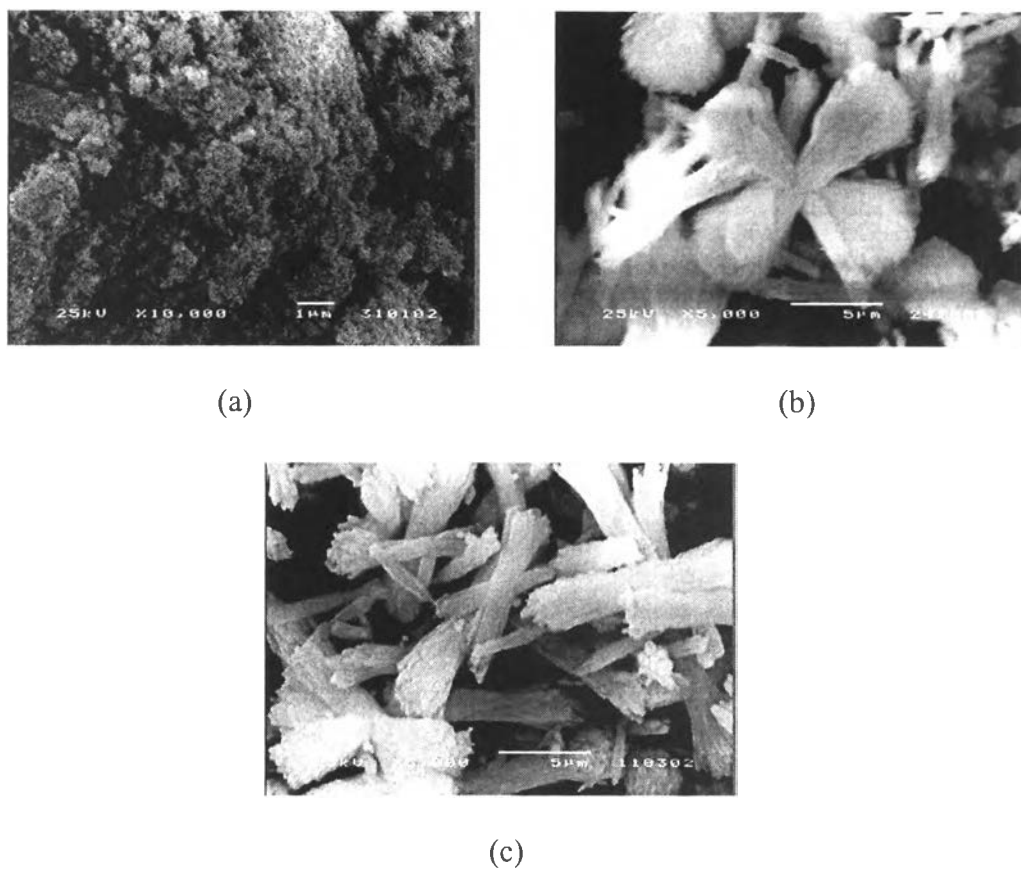
(b)

**Figure 6.3** Si:Al:K ratio of PCC-ZM-1 (a) and their crystal morphology (b)

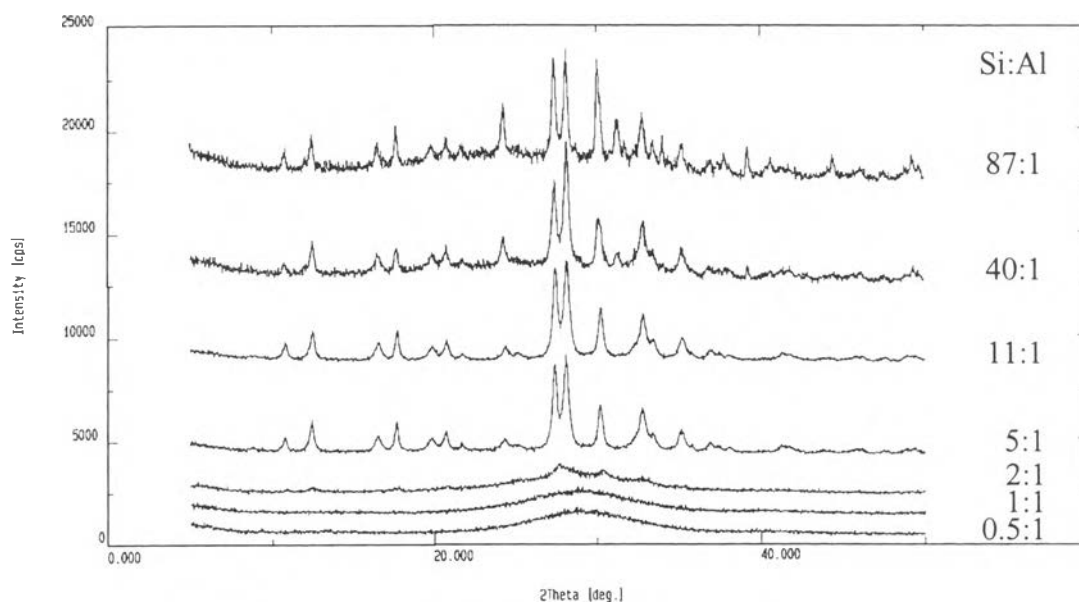


**Figure 6.4** Thermal property of PCC-ZM-1 synthesized from  $1\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and  $150\text{ °C}/300\text{ min}$

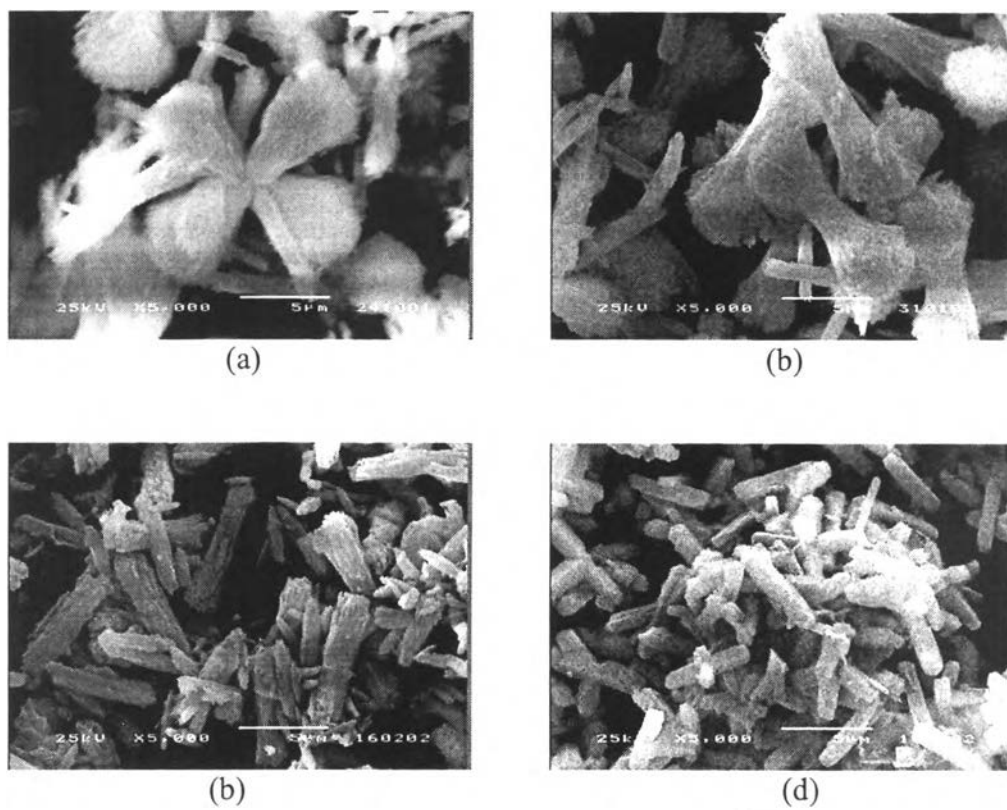




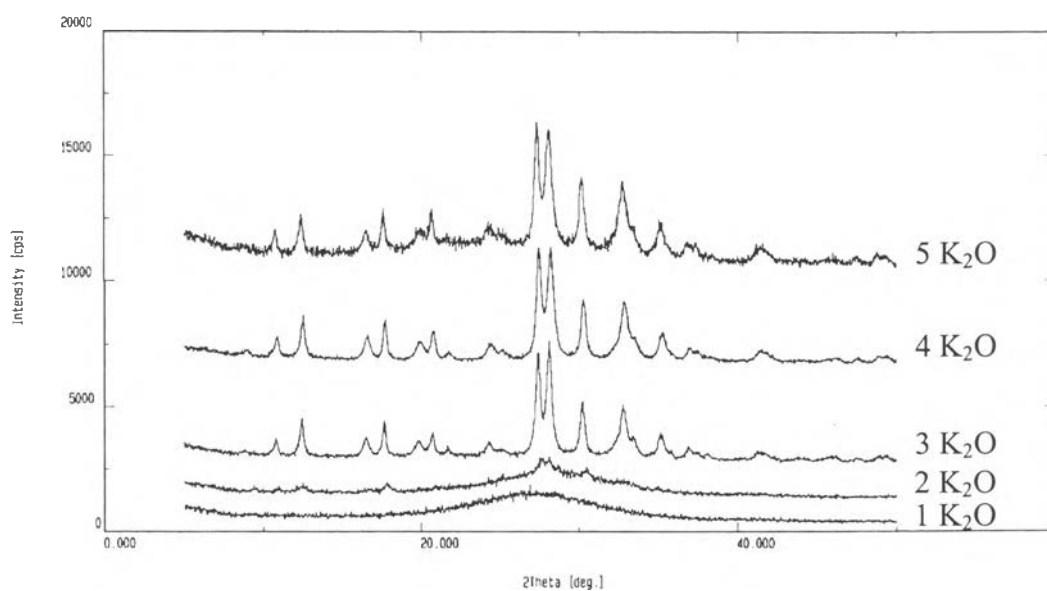
**Figure 6.5** Crystal morphology of PCC-ZM-1 synthesized from  $1\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$  and X °C/300 min; (a) 130, (b) 150 and (c) 170 °C



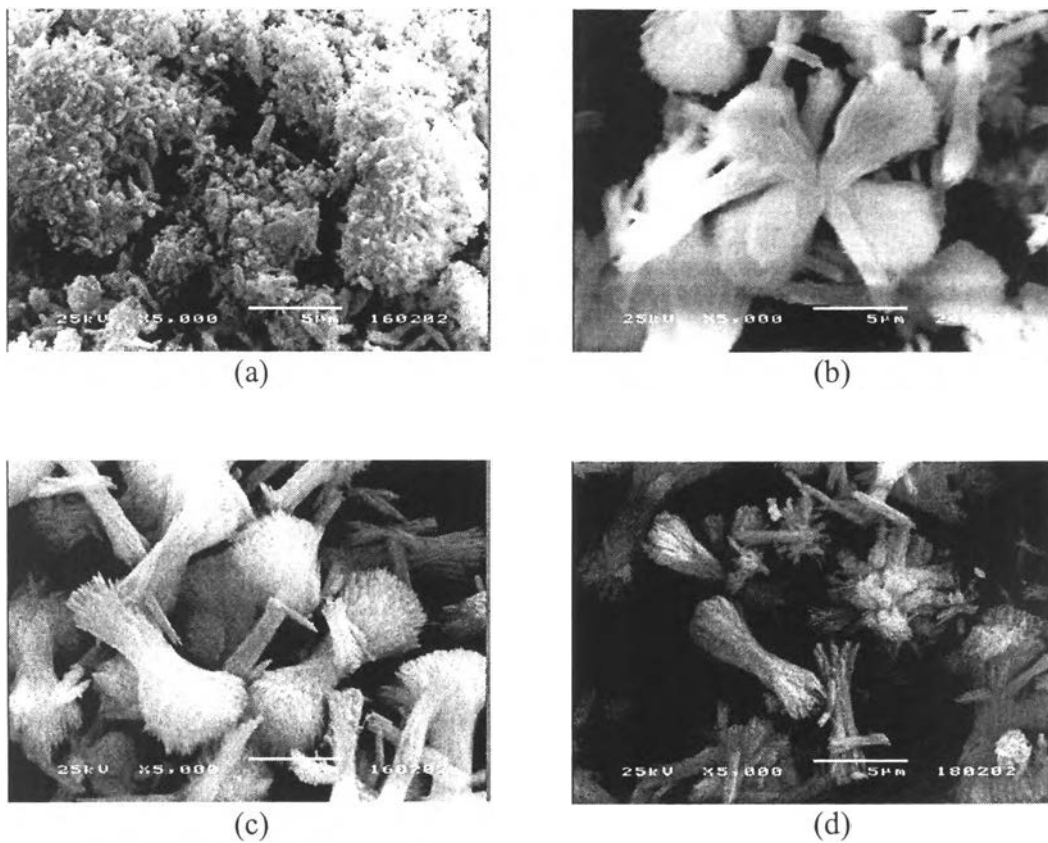
**Figure 6.6** Effect of Si/Al loading ratio on K-aluminosilicate synthesized from  $1\text{SiO}_2:X\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  ( $X = 1.0 - 0.1$ ) and  $150\text{ }^\circ\text{C}/300\text{ min}$



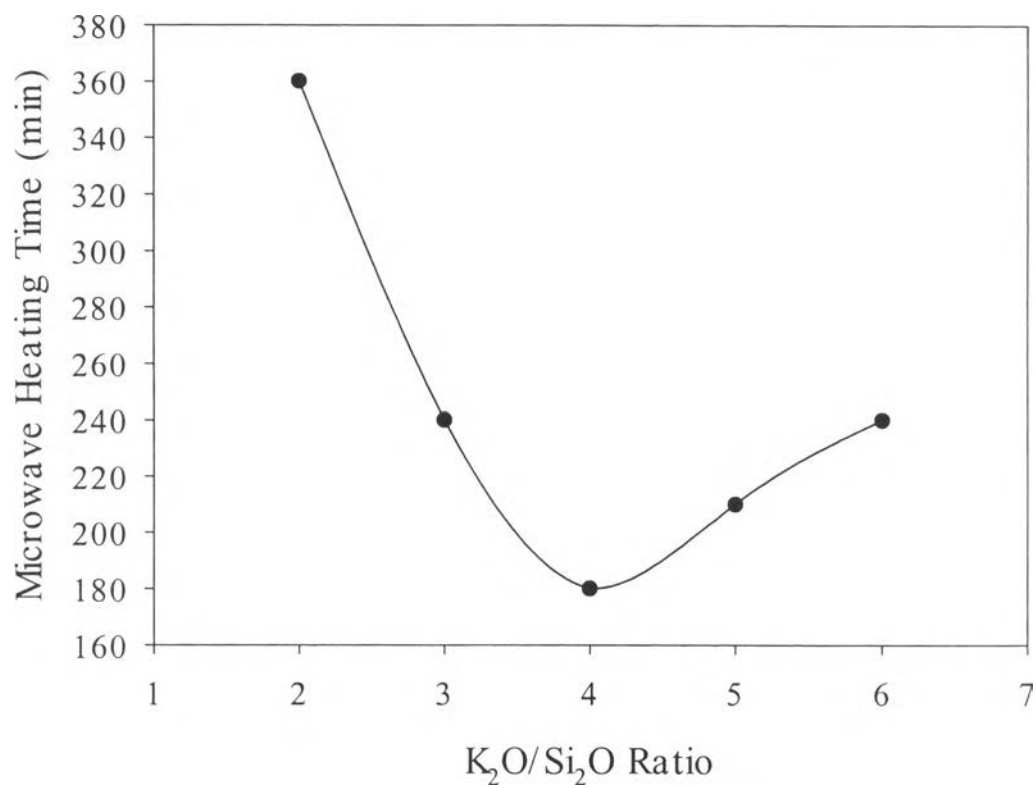
**Figure 6.7** Crystal morphology of K-aluminosilicate synthesized from  $1\text{SiO}_2:X\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and  $150^\circ\text{C}/300\text{ min}$  which at Si/Al ratio of (a) 5 (b) 11, (c) 40 and (d) 95



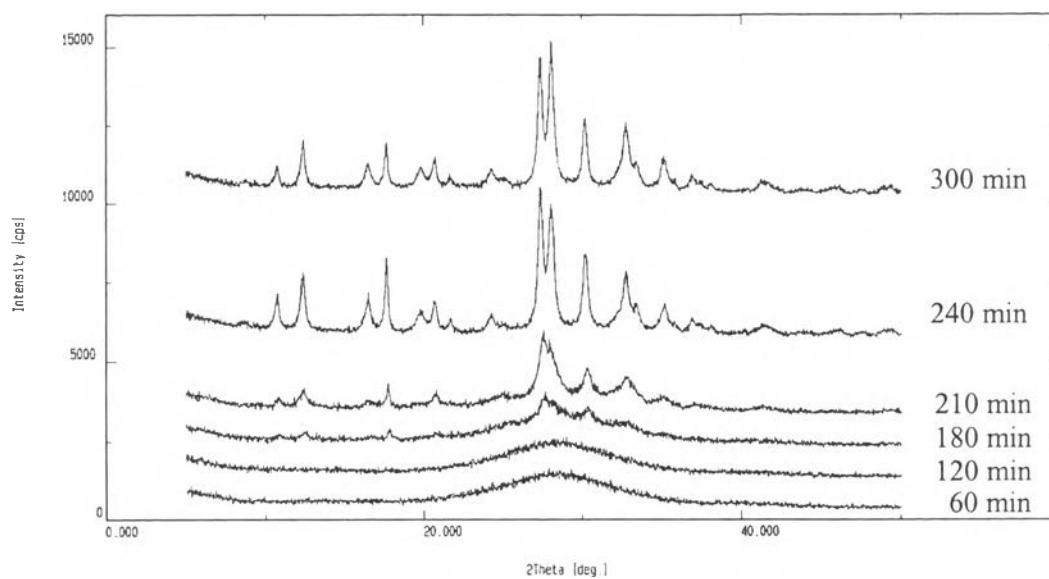
**Figure 6.8** Effect of K<sub>2</sub>O concentration on K-aluminosilicate synthesized from 1SiO<sub>2</sub>:0.1Al<sub>2</sub>O<sub>3</sub>:X K<sub>2</sub>O:410H<sub>2</sub>O (X = 1 - 5) and 150 °C/300 min



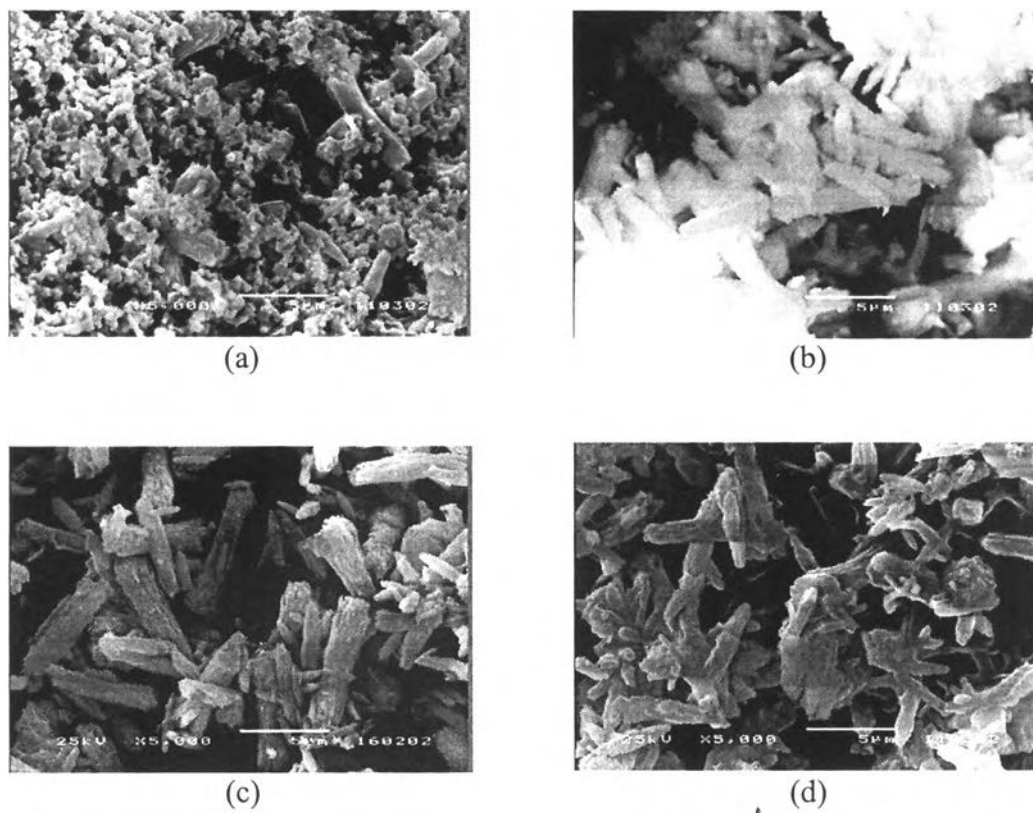
**Figure 6.9** Crystal morphology of K-aluminosilicate synthesized from  $1\text{SiO}_2 : 0.1\text{Al}_2\text{O}_3 : X\text{K}_2\text{O} : 410\text{H}_2\text{O}$  and  $150^\circ\text{C}/300\text{ min}$ ; X = (a) 2 (b) 3, (c) 4 and (d) 5



**Figure 6.10** Effect of K<sub>2</sub>O/SiO<sub>2</sub> ratio on microwave heating time by fixing at 1SiO<sub>2</sub>: 0.1Al<sub>2</sub>O<sub>3</sub>: X K<sub>2</sub>O:410H<sub>2</sub>O (X = 2 - 6) and 150 °C/300 min



**Figure 6.11** Effect of microwave heating time on K-aluminosilicate synthesized from  $1\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and  $150\text{ }^\circ\text{C}/\text{X min}$



**Figure 6.12** Crystal morphology of K-aluminosilicate synthesized from  $1\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  and  $150\text{ }^\circ\text{C}/\text{X min}$