CHAPTER IV

MFI ZEOLITE SYNTHESIS DIRECTLY FROM SILATRANE VIA SOL-GEL PROCESS AND MICROWAVE TECHNIQUE

4.1 Abstract

Silatrane was synthesized from the reaction of SiO_2 and triethanolamine using ethylene glycol as solvent under N_2 atmosphere. The obtained silatrane complex was further used as a Si source for MFI zeolite synthesis. The effect of Na^+, OH^-, and tetrabutyl ammonium hydroxide (organic template) concentration in the reaction mixture was studied. The reaction temperature was varied using the microwave heating technique. The effect of aging the reaction mixture at room temperature for varying times was also investigated. The rate of MFI formation decreases with increasing Na^+, decreasing OH^- or lower template concentration. Higher temperatures correlate to shorter aging and heating times. At fixed temperature, longer aging times lead to shorter heating times. It was found that a longer aging time is more important to achieve high crystallinity than the heating time.

4.2 Introduction

In recent years, synthesis of MFI (or ZSM5) zeolites has become one of increasing interests due to a variety of important applications. In particular, these zeolites can function either as a catalyst by itself or as a catalyst support. MFI is classified as a high silica zeolite, and is synthesized by interaction between a silicate precursor and an organic template, which acts as guest molecule in the structure of MFI. In some cases, the template can be omitted, for example in synthesis of a high aluminum MFI [1], whereas synthesis of a pure silica MFI cannot be achieved in the absence of an organic template. Several templates have been studied experimentally and via theoretical calculation [2-3]. The most effective organic templates are alkylammonium derivatives [4-6], and tetrapropylammonium salt (TPA) is the most common template for MFI synthesis, utilised in many published studies over the past few years [7-16].

Inorganic silica sources, such as fumed silica, silicic acid or sodium silicate, are typically used as zeolite precursors owing to their availability and low cost. De Moor *et. al.* (1999) have proposed a nucleation and growth mechanism for formation of MFI from a mixture of silicic acid and tetrapropylammonium hydroxide (TPAOH) and found that nanometer-scale primary units ("nanoblocks") containing a specific MFI topology are formed [10,14,17]. Nucleation involves the aggregation of these primary particles. Crystal growth occurs via stepwise addition of primary particles throughout the reaction period.

The use of organosilicate compounds, such as tetraethoxysilane (TEOS), in MFI synthesis has recently been demonstrated. Martens *et al.* (1999) studied the reaction of TEOS and concentrated TPAOH [11-13] and observed the formation of MFI nanoblocks, with the same MFI topology as reported in the study of De Moor et al [10,14,17]. One drawback, however, is that the reaction must be conducted under controlled humidity. The mechanism of nanoblock formation in the TEOS-TPA-H_2O system was explained, originating with hydrolysis of the organosilicate precursor followed by condensation reaction before the MFI primary units are formed [12,13].

From previous work, control of hydrolysis and condensation is the key to synthesis of mesoporous [18] and microporous [19] materials through sol-gel processing. However, TEOS is extremely susceptible to hydrolysis by water. Thus, it is of interest to use silatrane, a novel organosilicate which is more stable toward hydrolysis, and can be conveniently synthesized by the Oxide-One-Pot-Synthesis (OOPS) process.

Accordingly, we investigate a new synthetic route to MFI, using silatrane as the precursor and tetrabutylammonium hydroxide (TBAOH) as a template. The effect of OH^-, Na^+, H_2O and template concentration on the morphology of MFI crystals is explored. Other operating conditions, namely, aging time, heating time and temperature are also investigated.

4.3 Experimental

Materials

Fumed silica was purchased from Sigma Chemical. Triethanolamine(TEA, $N(CH_2CH_2OH)_3$) was supplied by Carlo Erba reagenti. Ethylene glycol (EG, $HOCH_2CH_2OH$) was obtained from J.T. Baker. Sodium Hydroxide (NaOH) and sodium chloride (NaCl) were purchased from EKA Chemicals and AJAX chemicals, respectively. Tetra-butyl ammonium hydroxide was obtained from Fluka Chemical AG. All these chemicals were used as received. Acetonitrile (CH3CN) was obtained from Lab-Scan Co., Ltd. and distilled prior to use.

Instrument

FTIR spectroscopic analysis was conducted using a Bruker Instrument (EQUINOX55) with a resolution of 4 cm^{-1}. The solid samples were mixed and pelletized with dried KBr. Mass Spectrometry was carried out with 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, and a cesium gun was used as an initiator. The mass range covered was from m/e= 20 to 3,000. Thermogravimetric analysis utilized a Perkin Elmer TGA7 at a scanning rate of 10 °C/min under nitrogen atmosphere and simultaneous thermal analysis (STA) was conducted by a Netzsch Instrument STA 409 at a scanning rate of 20 °C/min under nitrogen and oxygen atmosphere. Crystal morphology was characterised using a JEOL 5200-2AE scanning electron microscope. Crystal structure was determined using a Rigaku X-Ray Diffractometer at a scanning speed of 5 degree/sec using CuK as radiation and CuK as a filter. The working range was 3-50 theta/2 theta with 1 degree, 0.3 mm setting of divergent, scattering and receiving slit, respectively. Hydrothermal treatment by microwave heating technique was conducted using a MSP1000, CME Corporation (Spec 1,000w and 2450 MHz). The sample was heated in a Teflon tube using inorganic digestion mode with time-to-temperature programming.

Methodology

Silatrane Synthesis

Silatrane (Tris(Silatranyloxy-ethyl)amine or SiTEA) was synthesized following Wongkasemjit's method [20] by reacting 0.125 mol triethanolamine with 0.1 mol silicon dioxide using ethylene glycol as solvent at 200 °C under nitrogen atmosphere. The reaction was completed within 10 hr, and the reaction mixture was cooled to room temperature, before removing solvent by distilling under vacuum (10^{-2} torr) at 110 °C overnight. The resulting brownish white solid was washed three times with dry acetonitrile to obtain a fine white powder. The product was characterized using XRD, TGA, FTIR and FAB^+-MS.

MFI Synthesis

SiTEA equivalent to 0.25 g SiO_2 was dispersed in 5 ml of water and continuously stirred before adding TBAOH. Hydroxide and Na^+ concentration were controlled by adding calculated amounts of NaOH and NaCl, respectively. The formulation of SiO_2:TBA:OH^-: Na^+:H_2O was fixed at 1:0.1:0.4:0.4:114 to evaluate the effect of aging time, heating time and temperature. All reaction mixtures were aged at room temperature for various times with continuously stirring prior to heating to the reaction temperature. Different proportions of TBA, hydroxide ion, sodium ion and H_2O were studied to observe the effect on morphology of MFI crystals.

4.4 Results and Dicussion

Silatrane Synthesis

Oxide-One-Pot-Synthesis (OOPS) synthesis of silatrane was carried out under an inert atmosphere with continuous removal of water generated as by-product from the condensation reaction. Crystallized silatrane product was washed with dry acetonitile to remove non-reacting TEA and EG. The purified product was kept under vacuum to prevent hydrolysis by moisture though silatrane is more resistive to hydrolysis than other types of silicon alkoxide. Characterization by FTIR is shown in Table 4.1. XRD was carried out to confirm that silatrane is a crystalline product (Figure 4.1). TGA results show one mass loss transition at 400 °C and 18.36% ceramic yield. This value close to the theoretical yield of $Si((OCH_2CH_2)_3N)_2H_2$.

MFI Synthesis

In view of our use of a new silatrane precursor, it was necessary to study all formulation parameters and reaction conditions that might affect the formation of MFI.

Effect of Aging and Heating Times

From the experimental study, to obtain fully-grown crystals, the aging time and microwave temperature must reach at 84 hr. and 150 °C, respectively. Thus, to investigate the influence on MFI crystals of increasing the heating time, the aging time and microwave temperature were fixed at 84 hr and 150 °C, respectively. After 5 hr of heating, agglomeration of amorphous material was observed and very few of small crystals of 2 x 1 micron in orthorhombic shape were present, as shown in figure 4.2a. This was confirmed by XRD analysis which showed a broad amorphous peak around 23 /2theta together with some characteristic peaks of MFI at 7.95, 8.90 and 23.18 /2theta, see figure 4.3a. The broad amorphous XRD peak largely disappears when the sample mixture has been heated for 10 hr. However, there remains a little amorphous phase as most clearly seen in the SEM micrograph (figure 4.2b), which shows that crystals up to 6 x 2 micron are present, with small particles of amorphous material on their surfaces. The MFI crystal size increases with heating time, as evident in figure 4.2. However, the heating time does not have any effect on the crystal size after 15 hr of heating, as seen by comparing figures 4.2c and 4.2d.

As mentioned earlier, 84 hr aging time is required to produce perfect, fully-grown crystals. This result is illustrated in figure 4.4: when the mixture is aged for 36 hr, more amorphous phase is obtained (Fig. 4.4a); as the aging time is increased to 60 hr, no amorphous phase is observed, but the crystals are not fully-grown (Fig. 4.4b); after aging for 84 hr, fully-grown crystals are formed.

These results demonstrate that the aging process is important for synthesis of MFI from silatrane precursor. It is well known [21] that sol-gel processing via hydrolysis and condensation reaction causes the silicate precursor to polymerize and that the hydrolysis does not involve all the alkyl ligand initially, thus some organic component is present in the obtained polysilicate. This organic component can facilitate better mixing with the added organic template. The capability to enhance the insertion of organic template into the primary unit of MFI during hydrolysis allows more controllable condensation prior to primary unit formation. Mechanistic studies of MFI formation report that primary particles are always formed despite the fact that different types of precursor, either inorganic silicate [9-10] or organosilicate compound [11-13], are used. Therefore, we expect that primary particles exhibiting MFI structure are also formed in synthesis from silatrane.

In support of this, de Moor at al [14] find that these primary particles agglomerate to generate MFI nuclei, which is the initial step of crystal formation. Increased aging times result in higher concentrations of aggregates and faster crystallisation rates. This is consistent with our observation that more effective precursor conversion to crystals is obtained by increasing the aging time.

Effect of Temperature

It is well known that temperature strongly influences the formation of zeolites, using either organosilicate or inorganic precursors. The optimal temperature range depends on the Si/Al ratio. Pure silicate systems, such as MFI, tend to require higher temperatures, around 140° to 180 °C [22]. We studied the effect of temperature at 120°, 150° and 180 °C, using the sample ratio SiO_2:0.1TBA:0.4OH^-:0.4Na^+:114H_2O, an 84 hr aging time and 10 hr heating time. Selected SEM results are shown in figure 4.5. Heating at 120°C for 10 hr produces a morphology (Fig. 4.5a) and XRD result (not shown) similar to that produced by heating for 5 hr at 150 °C (c.f. Fig. 4.2a and Fig. 4.3a), i.e. mostly amorphous materials with few MFI crystals. However, when the heating time was extended to 20 hr, the amount of amorphous material decreases, and many small crystals of size around 1 micron are observed (figure 4.5b). These observations indicate that the temperature is too low for efficient MFI crystallization. At higher temperature (180 °C), larger crystals are obtained in shorter times (10 hr), as seen by comparing figure 4.5b with figure 4.5c.

It appears that MFI formation can be attained using a shorter heating and/or aging time with higher temperature. However, use of the microwave technique in zeolite synthesis at high temperature, especially at 180 °C, can degrade the organic template via Hoffman reaction, as reported by Arafat et al [7]. In our experiment, the clear colorless solution after thermal treatment at 180°C became reddish brown. However, perfect MFI crystals were also formed. It is possible that the template is degraded after the primary particles were formed, since, as explained by de Moor et al [10,14] the primary particles are present throughout the heating period and should have more stability to withstand the reaction temperature. These authors also found that the crystallization rate of MFI increases with reaction temperature, which correlates with our observation that the same crystal can be synthesized by shorter heating times at higher temperatures.

Role of Organic Template

Template molecules play a key role in zeolite synthesis, especially in the case of pure silicate or high silicate zeolites, such as MFI. Recently, many studies have been reported of the effect of organic template structure, including the number and length of alkyl groups [3, 5-6], physical shape [2], dimer and trimer derivatives [14] and organosilicate-containing template [23]. Most studies agree that the optimal template for MFI synthesis is tetrapropylammonium (TPA). However, Xin Li et al [23] showed that MFI can be synthesized using TBA as template, although several other studies indicate that TBA is a specific template for ZSM11. In the present study, we have succeeded in synthesizing MFI using a TBAOH template. This may be related to the fact that we have also used a different precursor, silatrane. For example, it is possible that, since silatrane generates a large organic ligand during hydrolysis, this makes the polysilicate more interact with organic template.

Kirschhock et al proposed that the structure of the primary unit of MFI, containing 33 silicate atoms per unit, interacts with one molecule of TPA [12]. Thus, we studied the effect of template concentration at TBA/Si = 0.017, 0.034, 0.1 and 0.15. Formulation variables were fixed at SiO_2:xTBA:0.4OH^-:0.4Na^+:114H_2O (x = 0.017, 0.034, 0.1 and 0.15), and reaction conditions at 20 hr heating time, 150°C heating temperature and 84 hr aging time. As shown in the figure 4.6, the crystal size at TBA/Si = 0.017 is esentially the same size for TBA/Si = 0.034. However, at low TBA concentration more agglomerates of amorphous silicate are formed. This result is consistent with our observation that increased aging time enhances the crystallization rate. The concentration of template molecules is directly proportional to that of the primary units formed, which relates in turn to the number of nucleation sites.

Theoretically, complete conversion should be obtained at the stoichiometric equivalent ratio of 0.034 TBA/Si. However, our results indicate that some template may not participate in the formation of MFI, possibly due to interactions between template and organic ligands derived from the silatrane. As a result, MFI has to be synthesized at much higher template concentration. When TBA/Si = 0.1, there is no agglomeration, and the crystal size becomes smaller. Evidently, higher template concentration results in more nucleation events, resulting in smaller crystals. Thus the crystal size strongly depends on the concentration of organic template.

Effect of Sodium Ion

Here, we formulated the reaction mixture as SiO_2:0.1TBA:0.4OH^-:xNa^+:114H_2O where x = 0.3, 0.6, 0.9, with reaction conditions set at 84 hr aging time, 10 hr thermal treatment and 150 °C heating temperature. At 0.3 Na^+/Si, large crystals of MFI are formed together with a small amount of amorphous material.

Completely amorphous product was obtained at $Na^+/Si = 0.6$ and 0.9. This result is consistent with the conclusion of Koegler et al [8] that sodium ion and organic template have opposing effects on the formation of primary units. Sodium ions favor the formation of negatively charged SiO^- groups, whereas the organic template prefers when more hydrophobic Si-O-Si bonds are formed. Excess of sodium ion thus reduces the interaction between template and precursor, causing agglomeration of polysilicate to form dense amorphous phase.

On the other hand, lack of sodium ion in the system also results in less stabilization of nucleation step. We found the bigger crystal and more amorphous obtained in the lower sodium system (less than 0.3 Na^+/Si). The fact is that in the lower sodium system, less conversion from precursor to crystal was obtained, resulting in less nucleation which made the crystals grow bigger.

Effect of Hydroxide Ion

Hydrolysis of both inorganic and organic precursor occurs in the initial stages of the reaction, and strongly depends on the OH^-/Si ratio. Thus the role of hydroxide ion in zeolite synthesis is a major factor to be considered. We fixed the formulation at SiO_2:0.1TBA:xOH^-:0.4Na^+:114H_2O (x= 0.1, 0.2, 0.3, 0.4 and 0.5), with reaction conditions at 84 and 20 hr aging and heating time, respectively, 150°C. Selected SEM results are shown in figure 4.7. At 0.1 and 0.2 OH^-/Si, no MFI is formed. However, as shown in Fig. 4.7, crystals are observed from mixtures containing 0.3 to 0.5 OH^-/Si. The crystal size decreases with increasing OH^-/Si ratio.

At 0.1 OH^-/Si, a white cloudy gel was obtained after 84 hr aging time. Only at this condition was a gel formed. At 0.2 OH^-/Si, a white cloudy sol was obtained, and the reaction mixtures became clearer as the OH^-/Si ratio was further increased. The formation of gel becomes unfavorable during the aging period due to fast hydrolysis followed by condensation reaction with precursor, causing fewer interactions between precursor and TBA. Moreover, lower OH^- also causes fewer nucleation events, as can be seen by the larger crystal size and the presence of amorphous material in the SEM micrographs (figure 4.7a). At 0.5 OH^-/Si, the crystal size is smaller and some crystal fracture appears to occur, as shown in figure 4.7c. Possibly, dissolution of crystalline material under the highly basic conditions may take place under microwave conditions, as indicated in the work of Arafat et al [7]. The OH^-/Si ratio of 0.4 appears to be the optimum since no amorphous is observed (Fig. 4.7b).

Effect of Dilution

In this study, we conducted reaction using the same sample volume, but different water content. This avoids extraneous factors, which might occur, such as variations in the pressure created during heating. The reaction parameters were $SiO_2:0.1TBA:0.4OH^-:0.4Na^+: xH_2O$ (x = 85, 150 and 250), 84 hr aging time and 150°C for 20 hr. The SEM results are shown in the figure 4.8. Smaller crystals were synthesized at the most concentrated condition of $H_2O/Si = 85$, and elongated crystals were obtained at the more dilute condition ($H_2O/Si = 250$). However, we point out that at very high dilution ($H_2O/Si = 450$, not shown), no crystallized product was obtained presumably due to a decrease in nucleation rate from fewer collisions between primary units. Therefore, more concentrated conditions give smaller crystal sizes due to a higher nucleation rate. The observation from SEM that the crystals grow into longer rectangular shapes on dilution, compared to the square shapes more commonly found is not understood at present.

4.5 Conclusion

Silatrane complex SiTEA was successfully synthesized via the OOPS process and used as a silica source for the MFI synthesis. Aging time of the reaction mixture prior to heating plays a very important role in the formation of MFI. Complete conversion of SiTEA to MFI crystals was obtained with longer aging times. However, heating time also has an effect on SiTEA conversion, a longer heating time resulting in better conversion. Higher temperatures can be applied to curtail aging and heating times. As for the effect of OH^-, Na^+, H_2O and template concentration, less perfect crystals of MFI are obtained when increasing Na^+, decreasing OH^-, or decreasing TBA concentration. The shape of MFI crystals appears to depend on the level of water present.

4.6 Acknowledgements

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4.7 References

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CAPTIONS OF TABLE AND FIGURES

Table 4.1	Peak positions and assignments in the FTIR spectrum of synthesized silatrane.
Figure 4.1	XRD spectrum of synthesized silatrane.
Figure 4.2	Effect of heating time on reaction of SiO_2: 0.1 TBA: 0.4 OH^-: 0.4 Na^+: 114 H_2O at 150°C, after 84 hr aging time a) 5 hr, b) 10 hr, c) 15 hr and d) 20 hr.
Figure 4.3	XRD patterns of products formed from reaction of SiO_2: 0.1 TBA: 0.4 OH^-: 0.4 Na^+: 114 H_2O at 150°C after 84 hr aging time, at heating times of: a) 5 hr b) 10 hr c) 15 hr and d) 20 hr
Figure 4.4	Effect of aging time on morphology of products formed from SiO_2: 0.1 TBA: 0.4 OH^-: 0.4 Na^+: 114 H_2O mixtures with heating for 20 hr at 150°C: a) 36 hr, b) 60 and c) 84 hr.
Figure 4.5	Effect of temperature on products formed from SiO_2: 0.1 TBA: 0.4 OH^-: 0.4 Na^+: 114 H_2O after 84 hr aging time and heating at: a) 120°C for 10 hr, b) 120°C for 20 hr and c)180°C for 10 hr.
Figure 4.6	Effect of template concentration on products formed from SiO_2: x TBA: 0.4 OH^-: 0.4 Na^+: 114 H_2O after aging for 84 hr and heating at 150°C for 20 hr: TBA/Si ratios, x, are a) 0.017, b) 0.034, c) 0.1 and d) 0.15 with aged
Figure 4.7	Effect of hydroxide concentration on products formed from SiO_2: 0.1 TBA: x OH^-: 0.4 Na^+: 114 H_2O after aging for 84 hr and heating at 150°C for 20 hr: OH^-/Si ratios, x, are a) 0.3, b) 0.4 and c) 0.5.
Figure 4.8	The effect of dilution on products formed from SiO_2: 0.1 TBA: 0.4 OH^-: 0.4 Na^+: xH_2O, after 84 hr aging time and heating at150°C for 20 hr: H_2O/Si ratios, x, are a) 85, b) 150 and c) 250.

Table 4.1

Peak Positions (cm^{-1})	Assignments
3100-3700	b, ν O-H
2800-3000	s, ν C-H
2750-2670	w, NR_3 salt (Si←N)
1445, 1459, 1493	m, δ C-H
1351	w, ν C-N
1276	m, ν C-O
1040-1180	b & vs, ν Si-O
786	vs, δ Si-O-C
735	s, δ Si-O-C
576	w, Si←N

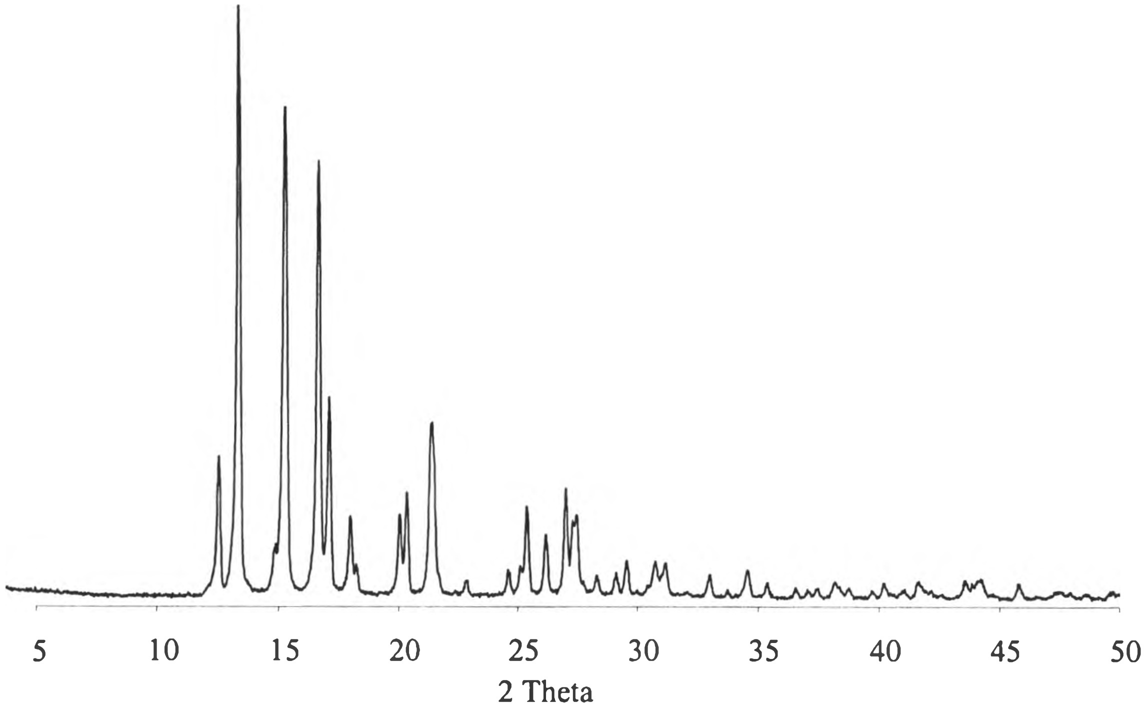
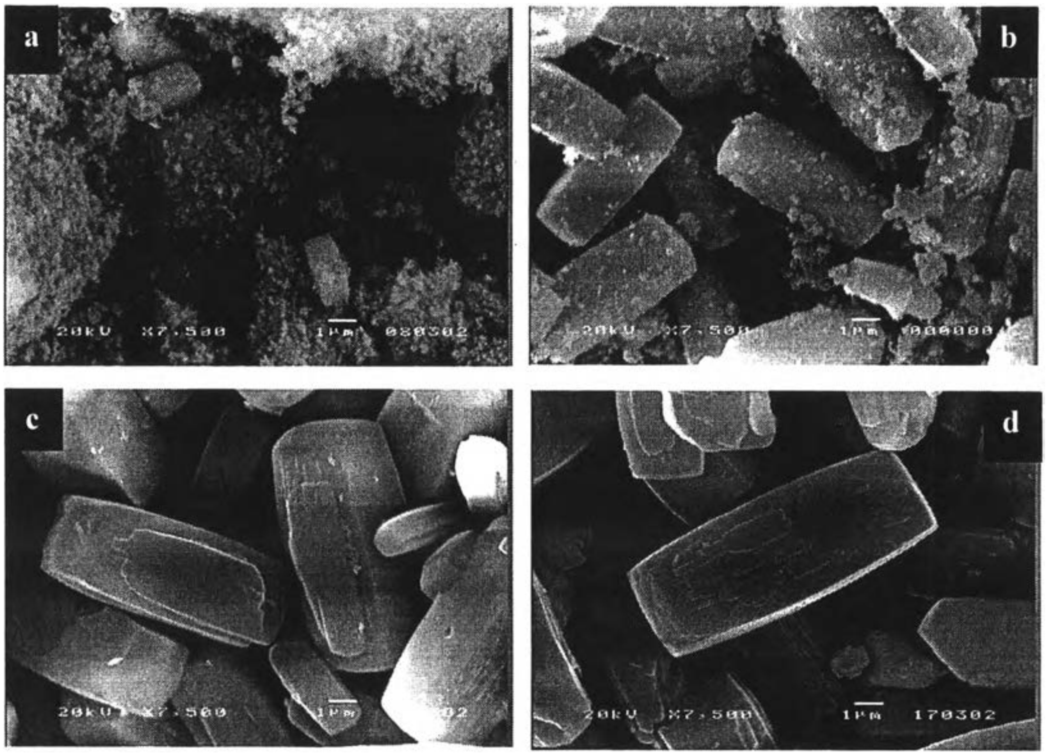


Figure 4.1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20kV X7,500 1μm 080302
b
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d
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Figure 4.2

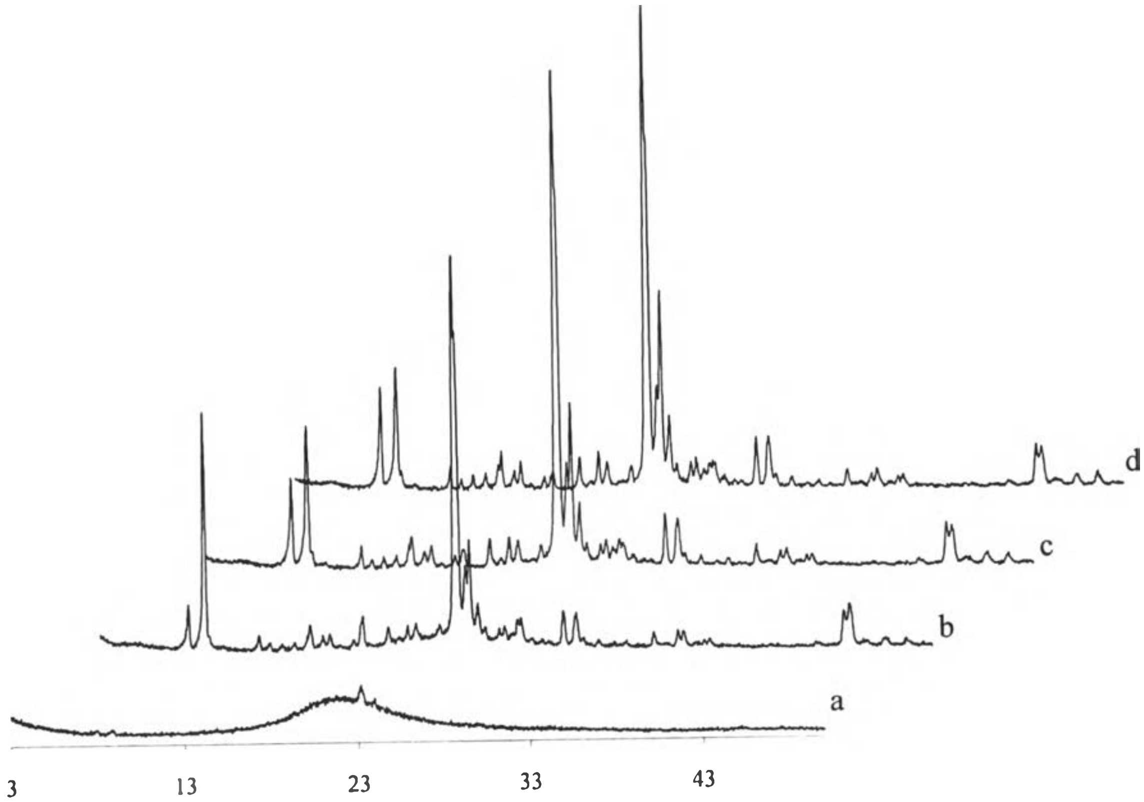


Figure 4.3

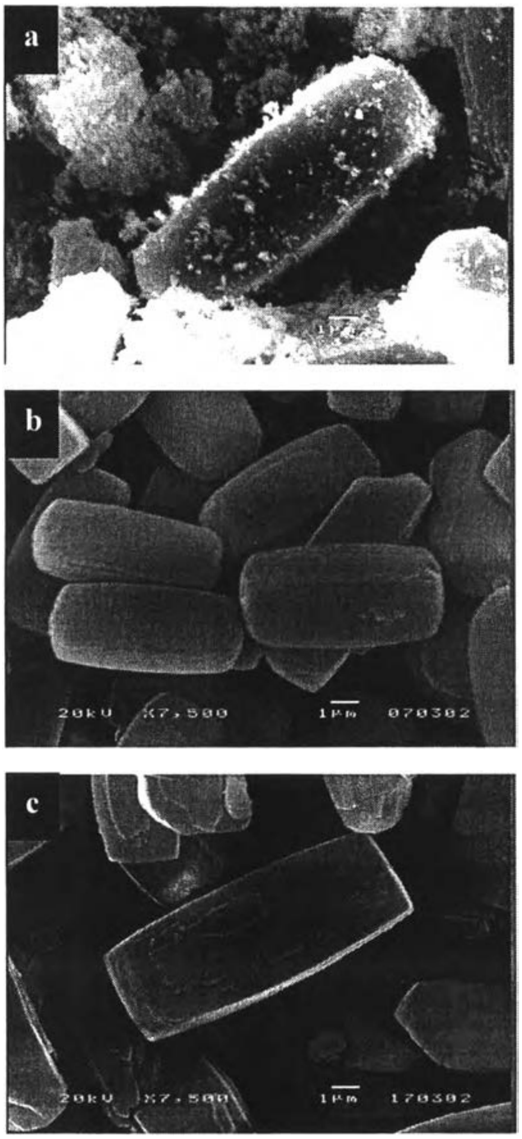


Figure 4.4

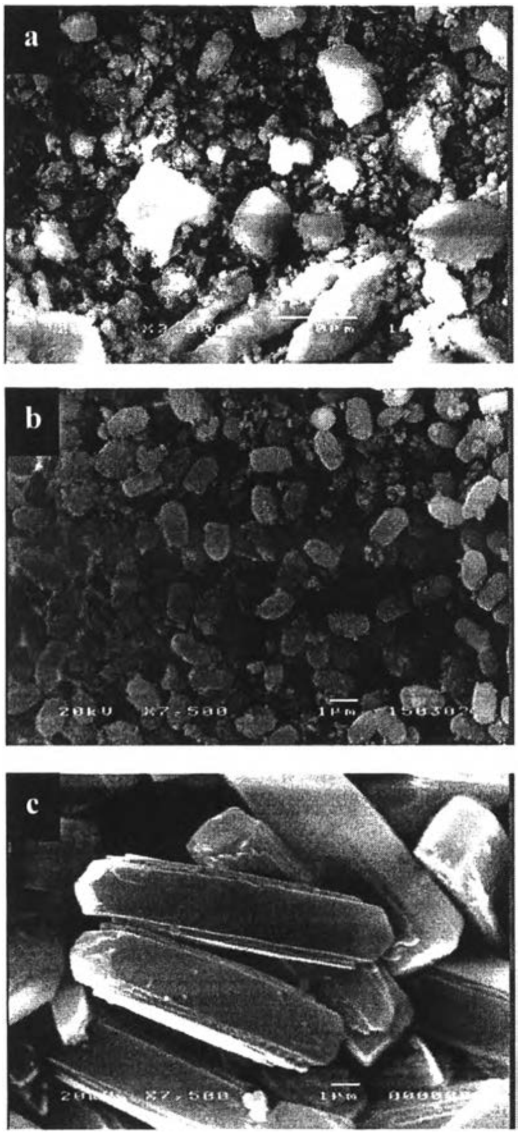
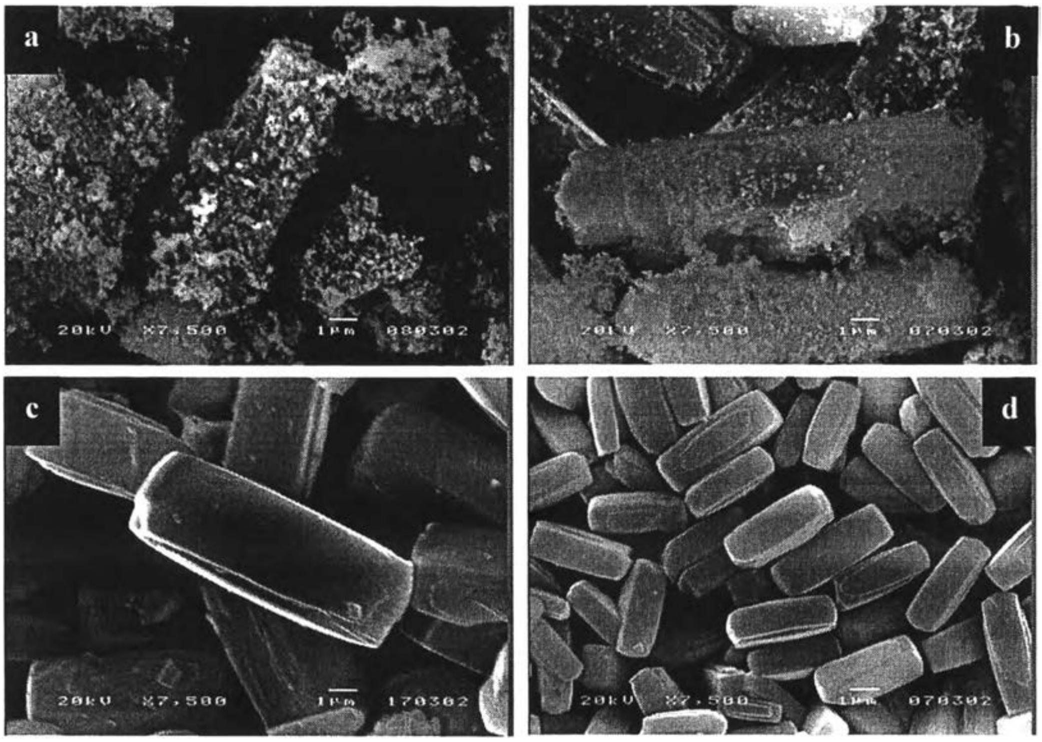


Figure 4.5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20kV X7,500 1µm 080302
b
20kV X7,500 1µm 070302
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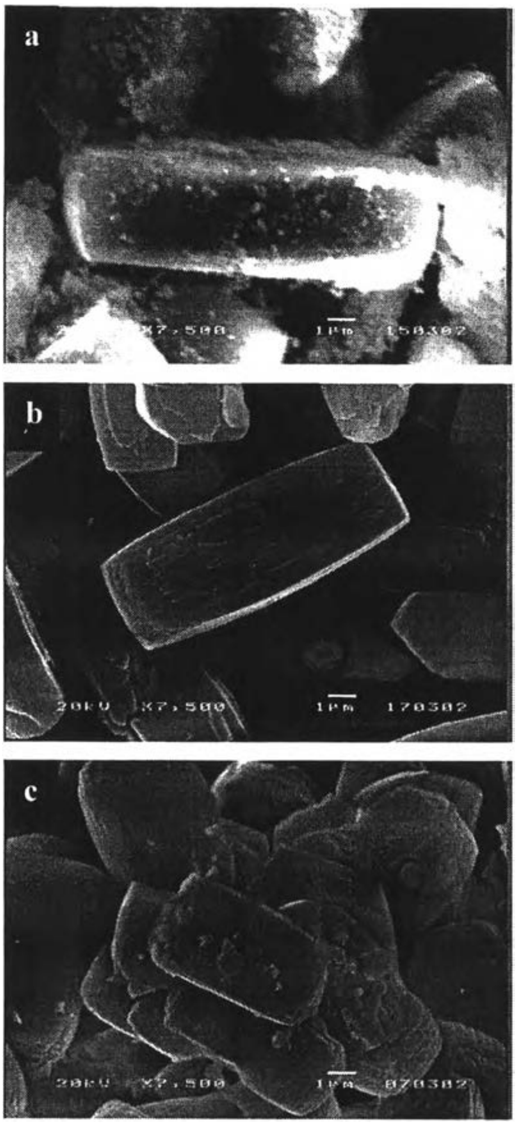
d
20kV X7,500 1µm 070302

Figure 4.6


a
X7,500
1μm
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b
20kV
X7,500
1μm
170302
c
20kV
X7,500
1μm
070302

Figure 4.7

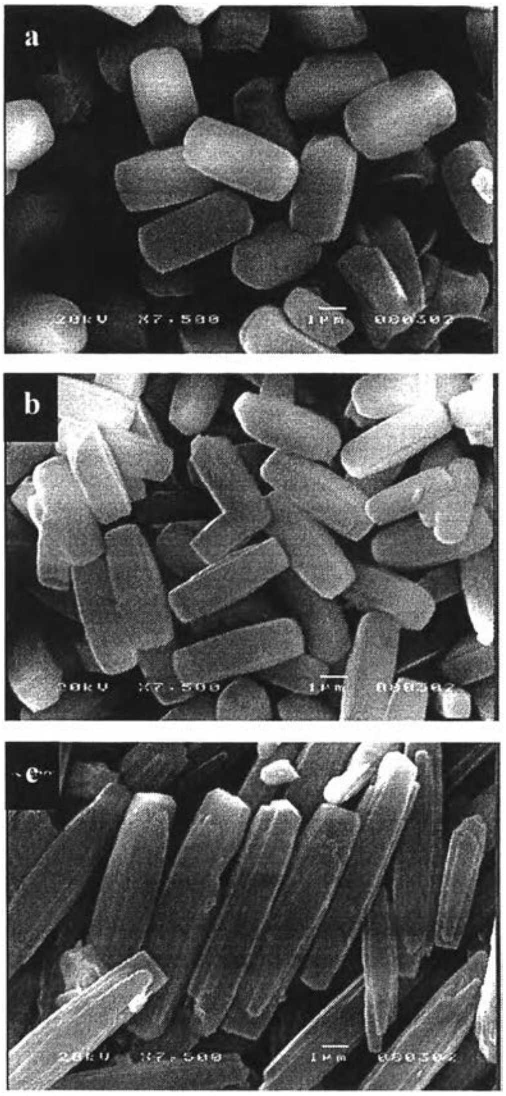
a
20kV X7,500 1μm 080302
b
20kV X7,500 1μm 080302
c
20kV X7,500 1μm 080302

Figure 4.8