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Hydrothermal Synthesis of Nanocrystalline Zeolite using Clear Solution

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ABSTRACT

Nano size particles such as nanocrystalline zeolites have unique properties relative to conventional micrometer sized zeolite crystals. The reduction of particle size to the nanometer scale leads to substantial changes in properties of zeolite which make them as promising materials for many applications. Nanocrystalline zeolite A, silicate-1 and ZSM-5 were successfully synthesiszed at temperature of 80-150^{0}C using clear solution in the presence of organic templates. Values of 1.46, 3.06, 4.59 and 6.79 are effective Si/Al ratio to synthesis LTA zeolite. Further, high Si/Al ratio of 30, 40 and 60 were used for ZSM-5 synthesis. The product could be obtained at 1-5 day for zeolite A and ZSM-5 while silicate-1 (aluminum free) could be obtained at 5-9 day. It is proved that zeolite yields increased with increasing temperature, time, Si/Al ratio and organic template. Moreover, TEOS and Ludox LS as silica sources in the silicate-1 synthesis were found to influence the particle size. TEOS makes the zeolite particle smaller than Ludox LS. Two stage synthesis conducted on silicate-1 crystallization could decrease time and increase yield. However it is found that the average particle size was slightly higher than that in one-stage synthesis.

Key words: Nanocrystalline zeolite, clear solution, organic template, one-stage synthesis

1. INTRODUCTION

Nanozeolites are crystalline aluminosilicates with molecular dimension in the range of 10-1000 nm of the particle size (Mintova, 2003). Nanozeoilites have higher external surface area and reduced diffusion path lengths due to smaller particle size. The reduction of particle size to the nanometer scale leads to substantial changes in properties of zeolite which make them as promising materials for many applications.

Zeolite nanocrystals are usually synthesized under hyhrothermal condition using clear aluminosilicate solution, usually in the presence of organic compounds as templates such as tetramethylammonium (TMA) and tetrapropylammonium (TPA) (Zhan, et al. 2001). Further, Cundy and Cox (2004) reported aluminosilicate zeolites synthesized under hydrothermal condition from reactive gels in alkaline media at temperature of about 80^{0}C and 200^{0}C and most high Si/Al ratio of zeolites (>10) are synthesized using organic templates, which have to be removed from the zeolites structure by calcinations. Mintova (2003) reported the synthesis of nano size zeolites including nanozeolite A (LTA), nanozeolite Y (FAU), nanozeolite silicate-1 (MFI) and nanozeolite beta (BEA) at temperatures lower than 100^{0}C with synthesis time up to 400 hours. The successful synthesis of nanozeolite A was also reported by Rakoczy and Traa (2003) who synthesized the materials at temperature of 80^{0}C with initial Si/Al ratios of 3.05, 4.03, 5.03, 6.99 and 7.89 and particle sizes in the range of 50-100 nm. The other researchers Persson et al (1994) reported the success of nanozeolite silicate-1 synthesis with average particle size of less than 100 nm at temperature of 155^{0}C in 29 hours. Moreover, Grieken et al (2000) reported the synthesis of nanocrystalline ZSM-5 at 170^{0}C for 24 hours with 10-100 nm particle sizes. The initial SiO_2/Al_2O_3 of molar ratio used in the synthesis process is 60. With the similar procedure to Grieken et al, Song et al (2004) synthesized nanocrystalline ZSM-5 at temperature of 165^{0}C with Si/Al ratio of 20. The obtained ZSM-5 particles were 15-60 nm for 120 hours synthesis time.

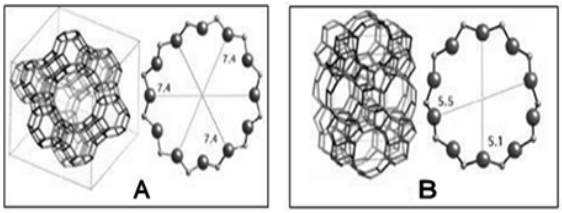

Figure 1. Zeolite framework and channel dimension (pore opening), (A) LTA, (B) MFI

(http://www.iza-stucture.org, retrieved: 10 August 2007)

Many other researchers reported the success of nanozeolite synthesis which indicate the interesting and promising prospect of nanozeolite technology (Tosheva & Valtchev, 2005). Figure 1 shows the description of zeolite framework and channel dimension of LTA, FAU and MFI.

This article reports experimental studies on synthesis of nanocrystalline zeolite A, silicate-1 and ZSM-5 under hydrothermal condition using clear solution in the present of organic template. Some parameters in synthesis process such as the effects of time, temperature, initial Si/Al ratio, and specific reactant will be evaluated.

2. METHODS

2.1 Synthesis of nanozeolite A (LTA)

In preparation of LTA, two typical solutions have been deployed, namely solution-1 and solution-2. The solution-1 is composed of aluminum tri-isopropoxide ($Al(OiPr)_3$, 99.99%, Sigma-Aldrich) dispersed in distillated water and sodium hydroxide (NaOH, 1M). Furthermore, the solution was vigorously stirred for an hour. After that, TMAOH (25 wt.% in water, Sigma-Aldrich) was added. The solution-2 is composed of Ludox LS colloidal silica (30 wt.%, Sigma-Aldrich) and distilled water. Next, the solution-1 and solution-2 were mixed under constant stirring to produce a clear synthesis solution. The molar composition of various synthesis solutions are shown in Table. 1.

Table 1. Molar composition of zeolite A synthesis solution

SAMPLE	Si/Al	MOLAR COMPOSITION
LTA-1	1.46	$2.92SiO_2$: Al_2O_3: $0.29Na_2O$: $0.58(TMA)_2O$: $493.57H_2O$
LTA-4, LTA-5, LTA-6, LTA-19, LTA-20, LTA-21	3.06	$6.12SiO_2$: Al_2O_3: $0.29Na_2O$: $2.24\ (TMA)_2O$: $345.36H_2O$
LTA-8, LTA-9, LTA-10, LTA-11, LTA-23, LTA-24, LTA-25, LTA-26	4.59	$9.18SiO_2$: Al_2O_3: $0.29Na_2O$: $2.8\ (TMA)_2O$: $458.9H_2O$
LTA-14, LTA-15, LTA-16	6.79	$13.58SiO_2$: Al_2O_3: $0.23Na_2O$: $4.48(TMA)_2O$: $538.59H_2O$
LTA-28, LTA-29, LTA-30, LTA-31	3.06	$6.12SiO_2$: Al_2O_3: $0.25Na_2O$: $2.24(TMA)_2O$: $359.73H_2O$
LTA-33, LTA-34, LTA-35, LTA-36	4.59	$9.18SiO_2$: Al_2O_3: $0.31Na_2O$: $2.80\ (TMA)_2O$: $461.58H_2O$

Then, the solution was put in a stainless steel autoclave (100 ml) for crystallisation at temperature of 80^0C, 120^0C and 150 ^{0}C in an oven. The autoclave was subjected to varying crystallisation time, from 1 day to 5 days. The product was then separated from solution in a centrifuge with 4700 rpm for 3 hours (Heraeus Multifuge 1s Kendro). Repeated rinsing and centrifugation for 4 times were done to purify the product and finally filtration was employed to obtain the nanozeolite A product. next, the product was dried at 120 ^{0}C for 24 hours and then calcined at temperature of 550 ^{0}C for 3 hours.

2.2 Synthesis of nanozeolite silicate-1 (MFI)

Synthesis solution was made by adding tetrapropylammonium hydroxide (TPAOH, Sigma Aldrich) into silica sources (Ludox LS or TEOS) and followed by strong mixing. The solution was then added by distilled water and ethanol. If the silica source is TEOS (tetraethyl orthosilicate), the synthesis solution was shaken for 12 hours on a shaker (Certomat R Shaker from B. Braun). The synthesis mixtures with molar composition **2TPAOH: $0.15Na_2O$: $6SiO_2$: $532H_2O$: 51EtOH** (Ludox LS as silica source) and **2TPAOH: $0.15Na_2O$: 4.5Si: $382H_2O$: 51EtOH** (TEOS as silica source) were obtained. In the next step, the synthesis mixture was transferred to the crystallization vessel and heated in an oven at temperatures of 80^0C, 120^0C and 150^0C. After a certain synthesis time, the product was separated from mother liquor by centrifuge (Heraeus Multifuge 1s Kendro) at 4700 rpm for 2 hours. The solid phase was then rinsed up to 5 times and filtered. After that, the product was dried at 120 ^{0}C for 24 hours and then calcined at temperature of 600^0C for 3 hours. The temperatures of 80^0C and 120^0C were used for two stages synthesis period with varying of temperatures where 3, 4 and 5 days synthesis time were used at 80^0C as the first stage and another 1 day was used at 120^0C as the second stage.

2.3 Synthesis of nanozeolite ZSM-5 (MFI)

ZSM-5 synthesis was started by adding aluminum isopropoxide ($Al(OiPr)_3$) into the mixture of distilled water and tetrapropylammonium hydroxide (TPAOH). After a clear solution was obtained with stirring at room temperature, ethanol was then added into the solution followed by adding sodium hydroxide. And then, TEOS as silica source was added and stirred for 24 hours to ensure complete hydrolysis of TEOS. The molar composition of synthesis solution is depicted in Table 2.

Table 2. Molar composition of ZSM-5 synthesis solution

SAMPLE	Si/Al	MOLAR COMPOSITION
ZSM5-1, ZSM5-2	30	1.48TPAOH: $0.33Na_2O$: 0.49Al: 14.4Si: $656.83H_2O$: 97.68EtOH
ZSM5-3, ZSM5-4	40	1.48TPAOH: $0.33Na_2O$: 0.24Al: 9.6Si: $656.83H_2O$: 97.68EtOH
ZSM5-5, ZSM5-6	60	1.48TPAOH: $0.33Na_2O$: 0.24Al: 14.4Si: $656.83H_2O$: 97.68EtOH

Finally the synthesis solution was transferred into the bottle and put into an oven for crystallization at 90^0C. After a certain time, the samples were taken and separated by using the centrifuge at 4700 rpm for 2

hours. After that the samples were rinsed for 4-5 times. The next step is drying of the samples at 120^0C for 24 hours and calcinations at 600^0C for 3 hours.

2.4 Sample Characterization

X-Ray Diffraction (Siemen D501 XRD) and Scanning Electron Microscopy (SEM) were used to identify the synthesised product (structure and size). The specimens were mounted in standard plastic holder. The XRD patterns were recorded using Cu-radiation (40kV, 30mA) over a two–theta angular range of 5-70^0 at 0.04^0/2s. The measured diffraction patterns were interpreted by using the PDF Database sets 1-52, Jade6.0 and CSM search/match software. SEM (Philips XL30) was used to obtain a visual image of the samples with magnification in range of 30,000 to 75,000. The measurements of the particle size are done by using the software of Image pro plus version 4.1.0.0 onto the SEM images.

3. RESULTS

3.1 Synthesis of nanozeolite A (LTA)

Effects of crystallization time and temperature

The first investigation result obtained in this report shows that nanocrystalline zeolite A can be synthesised effectively at temperatures of 80^0C-150^0C with initial Si/Al ratio of 1.46, 3.06, 4.59 and 6.79. The following figure displays three XRD profiles of nanocrystalline zeolite A with initial Si/Al ratio of 3.06 at varying temperatures. According to the XRD patterns in Figure 2, zeolite A crystal can be obtained. This fact proves that the specific condition such as temperatures of 80, 120 and 150^0C, crystallization time of 5 days and initial Si/Al ratio of 3.06 is the effective condition to synthesis nanozeolite A crystal.

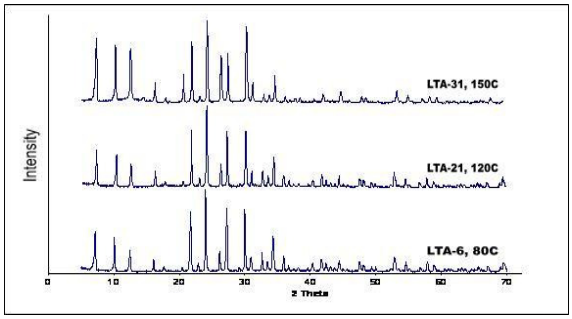

Figure 2. XRD patterns of nanocrystalline zeolite A at 80^0C, 120^0C and 150^0C

Nanocrystalline zeolite A products are also confirmed by SEM image where the visual structures shown in form of cubical which are similar to the zeolite A or linde A (LTA) crystal. Figure 3 describes the SEM images of LTA-6, LTA-21 and LTA-31 with average particle sizes of 370.04 nm, 384.26 nm and 521.65 nm, respectively. It can be seen from the pictures that higher crystallization time and temperature will result in the increase of average particle size. However, for LTA-6 and LTA-21 the difference of the average particle size is not significant.

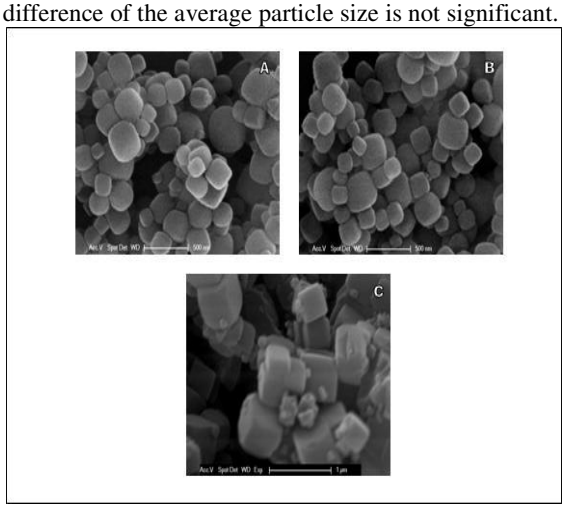

Figure 3. SEM images of nanocrystalline zeolite A at 5-day crystallization time, 3.06 initial Si/Al ratio, LTA-6, 80^0C (A), LTA-21, 120^0C (B) and LTA-31, 150^0C (C)

It is found that at temperatures of 80^0C and 120^0C no crystal can be recorded after 2 days. On the other hand, some LTA nanocrystal with average particle size of 104.8 nm can be obtained at 150^0C after 2-day crystallization. At 5-day crystallization time, the LTA crystals are 370.04 nm, 384.26 nm and 521.65 nm at 80^0C, 120^0C and 150^0C respectively. At 80^0C, the LTA nanocrystal grows at 104.7 nm, 124.85 nm and 370.04 nm for 3, 4 and 5 day crystallization time, respectively. A similar trend can also be seen for the temperature of 120^0C, the LTA crystal changes at 110.35 nm, 136.1 nm and 384.26 nm respectively for 3, 4 and 5 days. Moreover, at 150^0C, the crystals are at size of 104.8 nm, 127.65 nm, 400.37 nm and 521.65 nm for 2, 3, 4 and 5 days crystallization time, respectively.

The crystallization temperature also affects the yield of zeolite nanocrystal. Figure 4 shows correlation between temperature and yield of LTA nanocrystal. According to the curve, LTA yield increases with increasing crystallization time and also increase of temperature. On the other hand, some LTA products can be recovered at 150^0C after 2 days. The lowest LTA yield is 0.0964 g and the highest is 1.3761 g which were obtained at temperature of 150^0C for 2 and 5 days crystallization time. The highest yields based on silica used can be expressed at 61.16 %. This result is much better than Rakoczy & Traa (2003) who synthesised LTA nanocrystal at 80^0C with initial Si/Al ratio of 3.05 and obtained 11 % yield. This fact also proves that the higher crystallization temperature will produce higher zeolite yield and particle size.

The effect of initial Si/Al ratio

The investigation proves that initial Si/Al ratio influences LTA yield and particle size. Table 3 presents

particle size and product yield of LTA-6 and LTA-11 which were synthesised at 80^0C for 5 days of crystallization time. The table shows that at Na_2O/Al_2O_3 ratio of 0.3 and 0.0137 mole of $(TMA)_2O$ (Organic template), LTA-11 (Si/Al=4.59) has 1.1992 g yield, 20.01 % higher than LTA-6 (Si/Al=3.06) which has 0.9992 g yield. Similar result can also be shown from LTA-21 and LTA-26, which were synthesised at temperature of 120^0C for 5 days of crystallization. It can be seen that the increase of Si/Al ratio from 3.06 to 4.59 also resulted in an increase of LTA yield from 1.2032 g (LTA-21) to 1.3562 g (LTA-26) or by increased of 12.72 %.

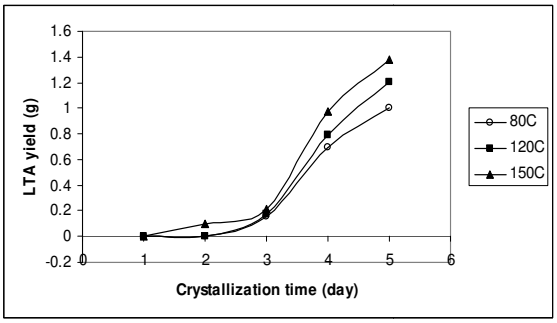

Figure 4. Effect of crystallization temperature on LTA yield with Si/Al ratio of 3.06

Table 3. Effect of initial Si/Al ratio on LTA yield and average particle sizes

Temp. (^{0}C)	Samples	Si/Al (mole/mole)	Yield (g)	Particle Size (nm)
80	LTA-6	3.06	0.9992	370.04
	LTA-11	4.59	1.1992	163.45
120	LTA-21	3.06	1.2032	384.26
	LTA-26	4.59	1.3562	181.79

Furthermore, initial Si/Al ratio also affects the average particle size of LTA nanocrystal. Table 3 shows that the increase of Si/Al ratio in the synthesis mixture will produce smaller particle size which can be ascribed to the less amount of aluminum content and slower crystal growth rate. At the temperature of 80^0C, LTA-11 (Si/Al=4.59) has the average particle size of 163.45 nm or 55.83% smaller than LTA-6 (Si/Al=3.06) which has 370.04 nm. The similar trend can also be found from LTA-21 and LTA-26. In those samples, the increase of Si/Al ratio from 3.06 to 4.59 results in decreasing of average particle size from 384.26 to 181.79 nm or a reduction of 52.69%.

In spite of a slight difference in Na_2O/Al_2O_3 ratio and organic template content (TMA cation) as is mentioned LTA samples above, synthesis of LTA nanocrystal at initial Si/Al ratio of 6.79 was also carried out. XRD pattern and SEM image show that the LTA nanocrystal can also be obtained. However, according to XRD result, the product also contains amorphous material (LTA-16). This is probably because of the high molar composition of Si/Al ratio (6.79) compared with other products such as LTA-1 (Si/Al=1.46), LTA-6 (Si/Al=3.06) and LTA-11 (Si/Al=4.59) and suggests that the large amount of silica source results in the precipitation of amorphous silica.

3.2 Synthesis of nanozeolite silicate-1 (MFI)

In this research, it was found that synthesis of silicate-1 nanocrystal takes longer crystallization time than crystalline zeolite A and ZSM-5. The silicate-1 nanocrystal product can be obtained after 5-day crystallization. In this report abbreviation SIL is used to describe silicate-1 nanocrystal products such as SIL-1, SIL-2, SIL-3 etc. The focuses on the effect of time, temperature (80^0C, 120^0C and 150^0C), silica source (Ludox LS and TEOS) and two-stage synthesis will be elaborated further.

Effect of crystallization time and temperature

It is well known that synthesis time and temperature directly affect the crystallization process. Higher product yield and bigger particle size will be obtained at longer synthesis time and higher temperature. This tendency could be found based on samples of SIL-9, SIL-10, SIL-11 and SIL-12 which were synthesised at 120^0C by using Ludox LS as silica source. XRD patterns of the samples are shown in Figure 5.

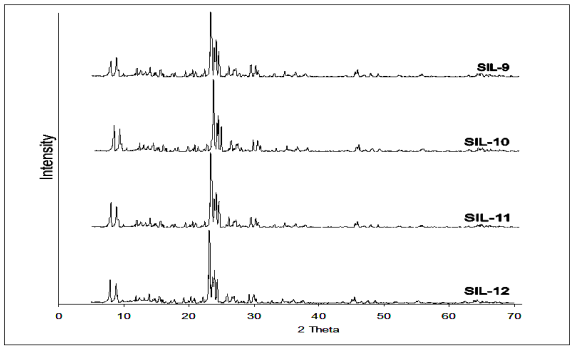

Figure 5. XRD patterns of silicate-1 crystals

The yields of SIL-9, SIL-10, SIL-11 and SIL-12 are 0.4065 g, 0.6263 g, 0.8028 g and 0.9957 g, respectively, with the particle sizes of 119.94 nm, 276.68 nm, 992.17 nm and 1678.54 nm. It can be seen that increase of crystallization time increases silicate-1 nanocrystal yields. And also similar trend regarding the average particle size with crystallization time can be seen from Figure 6, which shows the SEM image of silicate-1 nanocrystal. Further, the effect of temperature on synthesis can also be reported. At 9-day crystallization the silicate-1 product weights are 0.9077 g, 0.9957 g and 0.5267 g for temperature of 80^0C, 120^0C and 150^0C, respectively. Similar trend can also be found for crystallization time less than 9 days. At temperature of 150^0C it seems the products are lower

than others. The reason is due to the less amounts of reactants such as TPAOH, Ludox LS, distilled water and ethanol compared with those to other temperatures. At temperature of 150^{0}C only half amount of the reactants were used compared with 80^{0}C and 120^{0}C. The less reactants in the synthesis mixture result in the lower products of silicate-1 crystals. However, if the yield is calculated relative to the amount of used silica, it will get yields of 30.26 %, 33.19 % and 35.11 % for 80^{0}C, 120^{0}C and 150^{0}C, respectively, after 9 day, which means a increasing yield with increasing temperature.

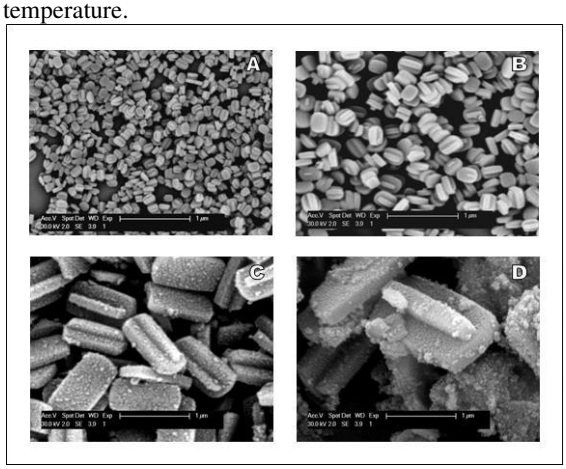

Figure 6. SEM images of silicate-1 nanocrystal at 120^{0}C, SIL-9, 5 days (A), SIL-10, 6 days (B), SIL-11, 7 days (C) and SIL-12, 9 days (D)

Other information, no silicate-1 nanocrystal yield can be obtained at 80^{0}C and 5-day crystallization time while 0.4065 g (13.55%) and 0.2155 g (14.37%) yields could be obtained at 120^{0}C and 150^{0}C, respectively. The yields of silicate-1 obtained in this experiment are quite low. The highest percentage of yield based on silica used is 35.11 % which is much lower than 61.45 % reported by Li et al (2000).

Effect of silica sources

The use of Ludox LS and TEOS as silica sources affects yield and average particle size. It is found that by using TEOS, the nucleation is faster and the particle size is smaller (Persson et al, 1994). However, in this research it is found that the yields of silicate-1 crystal are lower if Ludox LS was used as silica source. For instance, SIL-13 (TEOS as silica source) has 0.2169g yield or 16.07 % based on Si used. This is lower than SIL-9 (Ludox LS as silica source) which has 0.4065g or 29.46 % yield. Similar results can also be found at SIL-2 (Ludox LS) and SIL-6 (TEOS) which were synthesised for 6 days at 80^{0}C and they have 19.38% and 18.19% yields based on Si used, respectively. Furthermore, by using TEOS, 0.0745 g silicate-1 sample with average particle size of 50.26 nm (SIL-5) can be obtained after 5 days at 80^{0}C.

On the other hand no product can be obtained at the same condition by using Ludox LS. It can be meant that TEOS makes shorter nucleation and crystallization time than Ludox LS. The smaller average particle size by using TEOS compared with Ludox LS can be shown from SIL-9 and SIL-13 samples which were synthesised at 120^{0}C and 5-day crystallization and also other samples such as SIL-12 and SIL-16 at the same temperature and 9-day crystallization. The average particle size of SIL-9 and SIL-13 are 119.94 nm and 76.25 nm, respectively. It means, at the same conditions using TEOS can reduce 36.43 % of average particle size. Similar trend also can be seen for SIL-12 and SIL-16 which have average particle size of 1678.54 nm and 524.10 nm, respectively. For SIL-9 and SIL-12 samples which were synthesised at 5 and 9 days using Ludox LS, the average particle size is increased from 119.94 nm to 1678.54 nm. On the other hand, the particle size of SIL-13 and SIL-16 which were synthesised using TEOS at 5 and 9 days is increased from 76.25 nm to 524.10 nm. Thus, it is confirmed that TEOS can make smaller particle size than Ludox LS. The main reason that TEOS produces smaller crystal size is due to an average hydrodynamic diameter of 4 nm of TEOS smaller than Ludox LS of 15-19 nm (Li et al, 2000). Mintova and Valtchev (2002) also found similar results that the fast nucleation period and smaller particle size will be occurred if using TEOS. Li et al (2000) also reported the average crystal size could be reduced up to 66 % by using TEOS compared with Ludox LS. Further, at 100^{0}C crystallization temperature, Ludox LS gave a little bit higher yield than TEOS (60.6 % yield for TEOS and 61.45 % for Ludox LS).

Two stage synthesis

The two stage synthesis procedure involves synthesis at 80^{0}C and then 120^{0}C for a certain times. In this research, it is found that the two-stage synthesis has shorter crystallization time. For instance, samples SIL-25 (0.2613 g yield) and SIL-28 (0.0821 g) could be obtained in 4-day crystallization (3 days at 80^{0}C and 1 day at 120^{0}C). This result is better than any other samples synthesised at 80^{0}C, 120^{0}C and 150^{0}C, 5 days crystallization. However, the average particle size produced in the two stage synthesis is bigger than that in one stage synthesis. The samples SIL 30 and SIL-10 have the average particle size of 292.87 nm and 276.68 nm, respectively. This result is different from the observation reported by Li et al (1999). They found the same average particle size but a higher yield of silicate-1 in two stage synthesis. Further, this investigation shows that the effect of silica source on particle size using the two-stage synthesis is much similar to that in one stage synthesis, where TEOS gives smaller particle size while Ludox LS gives higher yield. This tendency can be reflected from samples SIL-27 and SIL-30 which used Ludox LS and TEOS as silica source, respectively.

3.3 Synthesis of nanozeolite ZSM-5 (MFI)

Nanocrystalline ZSM-5 was synthesised at 90^0C with initial Si/Al ratios of 30, 40 and 60. Because the crystallization temperature is not much higher so glass/polypropylene bottles at 500 ml volume were chosen as vessels. In the experiment, the product can be obtained after 2-day crystallization for all samples. For instance, the samples of ZSM5-1, ZSM5-3 and ZSM5-5 at Si/Al of 30, 40 and 60 have 0.1211 g, 0.1303 g and 0.1471 g yields, respectively. These results indicate a faster crystallization time compared with another experiment reported by Song et al (2004). Song et al could obtain the product after 5-day crystallization time with average particle size of 15 nm at 165^0C. According to Song's results, crystallization process seems slow. Some factors probably influenced this process such as sodium content and Si/Al ratio. Song et al used 0.16 of Na_2O/Al molar ratio as sodium content with Si/Al ratio of 20 and stainless steel autoclave as a vessel (crystallization reactor). This study used higher Na_2O/Al ratio (0.67) and Si/Al ratio (30, 40 and 60) than those reported in the above research. It is well known that the more sodium content in the synthesis mixture result in the higher crystallinity and shorter crystallization time. SEM images of ZSM5-1, ZSM5-3 and ZSM5-5 can be seen in Figure 7.

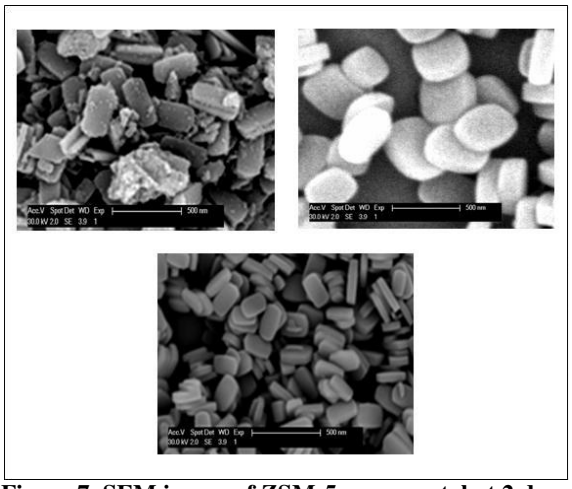

Figure 7. SEM image of ZSM-5 nanocrystal at 2 day crystallization time, Si/Al=30 (A), Si/Al=45 (B) and Si/Al=60 (C)

As mentioned above, the product yield increases by increasing Si/Al ratio. On the other hand, the increase of Si/Al ratio results in the decrease of average particle size. It can be seen that ZSM5-1, ZSM5-3 and ZSM5-5 with crystallization time of 2 days having the average particle size of 674.15 nm, 395.98 nm and 217.55 nm, respectively. Similar tendency can also be seen for ZSM5-2, ZSM5-4 and ZSM5-6 with 3 days crystallization. They have average particle sizes of 1078.77 nm, 752.56 nm, and 558.98 nm, respectively. Comparing ZSM5-1 with ZSM5-2, ZSM5-3 with ZSM5-4 and ZSM5-5 with ZSM5-6, the increase of particle size in the 24 hour interval times (from 2 to 3 days) are 60.02%, 90.05% and 156.94%. It also means that in the same interval of crystallization time, the increase of average crystal size follows the order of Si/Al ratio. Figure 8 shows the XRD patterns and SEM images of the samples.

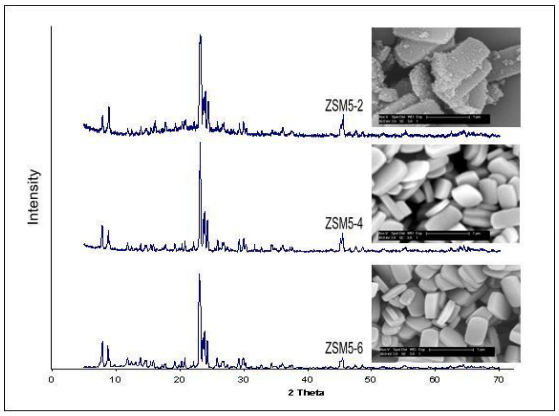

Figure 8. XRD patterns and SEM image of ZSM-5

4. CONCLUSIONS

Nanocrystalline zeolite A, zeolite silicate-1 and ZSM-5 could be successfully synthesised at temperature of $80\text{-}150^0$C. The product could be obtained at 1-5 day for zeolite A and ZSM-5 while silicate-1 could be obtained at 5-9 day. Beside temperature and time, zeolite nanocrystal syntheses are influenced by the molar composition of synthesis solution. Sodium content, initial Si/Al ratio and organic template composition are the important factors. The sodium content should be calculated thoroughly relative to alumina content to obtain the purity of the zeolite particularly on synthesis of zeolite A. It is proved that zeolite yields increased with increasing temperature, time, Si/Al ratio and organic template. Values of 1.46, 3.06, 4.59 and 6.79 are effective Si/Al ratio to synthesis LTA zeolite. Moreover, TEOS and Ludox LS as silica sources in the silicate-1 synthesis were found to influence the particle size. TEOS makes the zeolite particle smaller than Ludox LS. Two stage synthesis conducted on silicate-1 crystallization could decrease time and increase yield. However it is found that the average particle size was slightly higher than that in one-stage synthesis

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