CRYSTALLIZATION TEMPERATURE OF NaA ZEOLITE PREPARED FROM SILICA GEL AND ALUMINUM HYDROXIDE

Audy D. Wuntu[1], Vanda S. Kamu[1] and Maureen Kumaunang[1]

[1]*Jurusan Kimia Fakultas Matematika dan Ilmu Pengetahuan Alam*
Universitas Sam Ratulangi Manado

Diterima 08-01-2011; Diterima setelah direvisi 17-02-2011; Disetujui 25-02-2011

ABSTRACT

Wuntu, A. D. *et al*. 2011. Suhu kristalisasi zaolit NaA yang disintesis dari silica gel dan aluminium hidroksida.

Pengaruh suhu dalam tahap kristalisasi zeolit NaA telah dikaji dalam penelitian ini. Sintesis zeolit NaA dikerjakan pada kondisi hidrotermal konvensional menggunakan silika gel dan aluminium hidroksida sebagai bahan dasar dan kristalisasi dikondisikan pada suhu 60 ^{o}C, 75 ^{o}C, 90 ^{o}C, 105 ^{o}C, dan 120 ^{o}C. Kristalisasi zeolit NaA selanjutnya dianalisis dengan teknik spektroskopi infra merah. Hasil yang diperoleh memperlihatkan bahwa pada suhu 60 ^{o}C belum terbentuk kristal zeolit yang ditunjukkan dengan tidak adanya pita serapan yang menjadi karakteristik zeolit A pada spektra infra merah. Pita serapan khas zeolit A muncul pada spektra infra merah zeolit yang diperlakukan pada suhu kristalisasi 75 ^{o}C hingga 120 ^{o}C.

Kata kunci : kristalisasi, suhu, zeolite NaA, silika gel

INTRODUCTION

Zeolite is a crystalline aluminosilicate that can be classified into some crystalline structures such as A-type zeolite, sodalite, and faujasite based on the arrangement of SiO_4 dan AlO_4 tetrahedron. Each type of zeolite has typical pore size that depends on its structure and, as a result, acts as a molecular sieve. In addition, zeolite is used as adsorbent, catalyst, agent in waste water treatment, and as additive in detergent for its cationic exchange capacity. The role of zeolite is highly depend on the composition of Si/Al, crystalline structure, and particle size (Hosokawa and Oki, 2004).

A-type zeolite is one of the synthetic zeolites widely used in industrial applications, mostly as catalyst and adsorbent. A synthesis of this type of zeolit is generally performed under hydrothermal condition using reactive gel as raw material in alkaline media at the temperature in the range of 80 to 200 ^{o}C. First description of A-type zeolite synthesis was described by Milton (1959) concerning the synthesis at hydrothermal condition. Studies of aspects related to zeolite synthesis such as kinetics aspect and zeolite modification are then carried out by some researchers to meet the required products. Some of them are Dutta and Shieh (1986) and Hu and Lee (1990) which studied the effects of reactant composition and reaction temperature. The other researches related to the utilization of natural resources such as halloysite mineral (Donevska et al., 1985), tuff (Stamboliev et al., 1985) and husk rice (Nur, 2001) as raw materials for synthetic A-type zeolite were also accomplished.

All the researches include the synthesis at hydrothermal condition of conventional method using oven, or autoclave as heat sources. Such studies indeed showed that A-type zeolite could be produced from natural resources, but the use of impure material in the synthesis could increase the risk of volatile and toxic materials discharge (Robson, 2001) and of contamination (Kuhl, 2001). Chemicals used in the synthesis should then be highly concerned in relation to the possibility of contamination in the products. The contaminants could be undissolved in the crystallization and assist the nucleation of unwanted species. On the other hand, the dissolved contaminants could contribute the formation of silicate or metallosilicate in the solution or the precipitation of undissloved silicate species. arguments. Oleh karena itu lebih dianjurkan menggunakan zat kimia murni sebagai material awal dalam sintesis zeolit.

Wuntu (2002) had synthesized A-type zeolite using silica gel and aluminium hydroxide as raw materials. The effects of ageing and crystallization time on the crystallization degree of the zeolite was then studied by Wuntu and Tangkuman (2008) which showed that the synthesis could be carried out at crystallization time of 5 hours without ageing. To collect more information about the optimum condition for the synthesis of A-type zeolite, the data on hydrothermal temperature for the best crystallization degree should be obtained.

Korespondensi dialamatkan kepada yang bersangkutan :
[1]*Jurusan Kimia, FMIPA Universitas Sam Ratulangi Manado.*
Phone : -, E-mail : -

METHODOLOGY

Materials and Tools

Chemicals used in this experiment are p.a. grade of silica gel (Merck), aluimnium hydroxide (Merck), and sodium hydroxide (Merck). The primary equipment is infra red spectrophotometer Shimadzhu FTIR-8201PC.

Mixture of Silicate and Aluminate Solution

Silicate and aluminate solutions were prepared after the procedure described by Wuntu (2002). The amount of chemicals used could be varied in fixed composition to produce different volume of silicate and aluminate solutions.

1. Sodium silicate solution was prepared by dissolving NaOH in distilled water in the ratio of 0,48 g NaOH to 1 mL distilled water. This NaOH solution was then used to dissolve silica gel in the ratio of 1 mL NaOH solution to 0.1541 g silica gel in plastic apparatus. Soon after the gel dissolved, the solution was added with distilled water in the ratio of 1 mL akuades to 1,6 mL NaOH solution. The solution was then held to reach room temperature.
2. Sodium aluminate solution was prepared by dissolving NaOH in distilled water in the ratio of 0,48 g NaOH to 1 mL distilled water. This NaOH solution was then used to dissolve aluminium hydroxide in the ratio of 1 mL NaOH solution to 0.2 g aluminium hydroxide. Soon after the gel dissolved, the solution was added with distilled water in the ratio of 1 mL akuades to 1,6 mL NaOH solution. The solution was then held to reach room temperature.
3. Silicate solution was then added with aluminate solution in the volume ratio of 1:1 in plastic apparatus through stirring. Soon after the mixing, distilled water was added in the ratio of 2.6 mL distilled water to 1 mL of the solution through stirring. A gel was formed at this stage.

Determination of crystallization temperature

The gel formed at the previous stage was then divided into some closed plastic container and placed into oven at variable temperature in the range of 50 to 120 ^{o}C for 5 hours. 5 hours is the optimum crystallization time for zeolite formation according to this procedure (Wuntu dan Tangkuman, 2008). After the crystal formed, the zeolite was filtered and rinsed with distilled water until the neutral pH was reached. The crystal was then dried and characterized using infra red spectrophotometer.

RESULTS AND DISCUSSIONS

Mixing silicate and aluminate solution generates two phases, which are amorphous gel and super saturated solution, in equilibrium. Silicate and aluminate are arranged surrounding sodium cation in ionic environment. In this condition, silica sol is depolymerized in alkaline condition and the concentration of dissolved silica is increased. This, in turn, generates monomers which are polymerized into oligomer silicate species in the solution. It is postulated that the rate of dissolution is higher than that of nucleation and, therefore, the equilibrium between amorphous gel and super saturated solution is not changed. In the arrangement of crystal formed, it is assumed that aluminate tetrahedron is surrounded by silicate tetrahedron, and vice versa. Oxygen atoms in the crystal nuclei are positioned at the end of the tetrahedron. This oxygen is bonded to either silicone or aluminium atoms, and each silicone or aluminium atom in tetrahedral cage is bonded to four tetrahedral cages through oxygen bridge.

Infra red spectrum in the range of 4000-400 cm^{-1} of zeolite synthesized from silica gel and aluminium hydroxide at the temperature of 60, 75, 90, 105 dan 120 ^{o}C is showed in Figure 1. Vibration of zeolite structure produces absorption band typically to the range of mid and far infra red. This vibration is divided into external vibration and internal vibration of SiO_4^{4-} and SiO_4^{5-} tetrahedron (Karge, 2001). Internal vibration is produced from the vibration between atoms in a tetrahedron and external vibration is produced from the vibration between tetrahedrons.

Infra red spectrum depicted in Figure 1 shows strong absorption in the range of wave number of 1016.58 cm^{-1} to 995.35 cm^{-1} which is a characteristic of internal asymmetric stretching vibration O-Si-O or O-Al-O inside the SiO_4 and AlO_4 tetrahedron. A weak absorption band produced by symmetric stretching vibration O-Si-O or O-Al-O inside the SiO_4 and AlO_4 tetrahedron is observed at a lower frequency of 669.39 cm^{-1} to 665.50 cm^{-1}

Strong band absorption observed in the wave number range of 565.19 cm^{-1} to 553,62 cm^{-1} indicates the formation of double ring which is a characteristic of A-type zeolite crystal. On the other hand, band absorption observed in the wave number range of 468 cm^{-1} to 446,82 cm^{-1} is a characteristic of bending vibration and of 3460,61 cm^{-1} – 3402,74 cm^{-1} is a characteristic of hydroxyl on the surface of the solid.

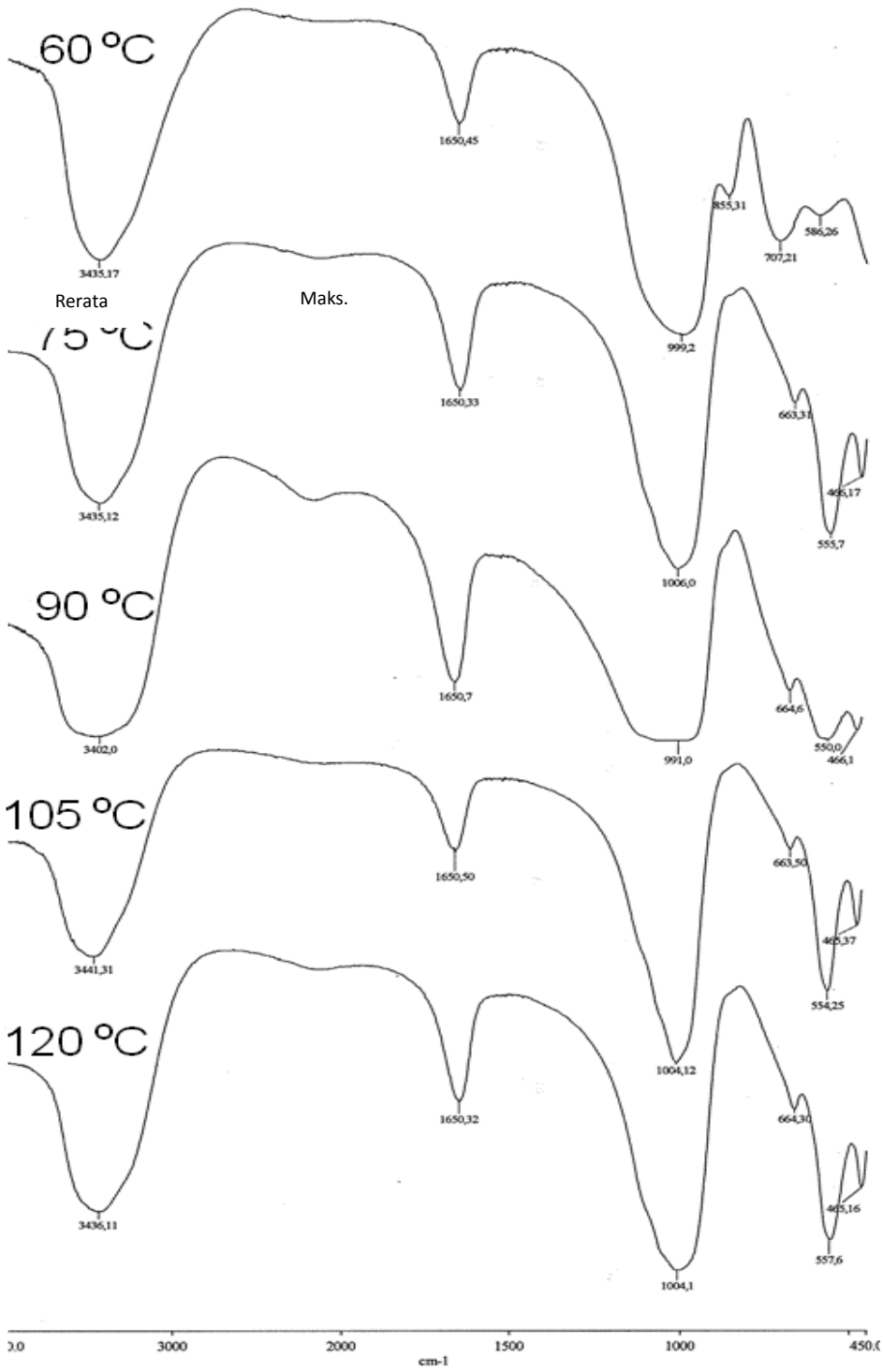

Figure 1. Infra red spectrum of A-type zeolite synthesized at 60, 75, 90, 105 and 120 ^{o}C.

All the bands which are the characteristics of A-type zeolite described above are not observed at the infra red spectrum of zeolite synthesized at the temperature of 60 ^{o}C. It seems that this temperature is too low for the formation of well crystallized zeolite in the period of time provided and crystallization time longer than five hours mayrequired. According to Milton (1959), A-type zeolite could crystallize at the temperature as low as 21 ^{o}C within six days and at the temperature of 100 ^{o}C in six hours. The bands are observed at the infra red spectrum of zeolite synthesized at the temperature of 75 to 120 ^{o}C (Figure 1) and this confirms that at 75 ^{o}C the A-type zeolite is well crystallized in five hours.

As a whole, the infra red spectrum of the zeolite solid synthesized at conventional hydrothermal condition (Figure 1) shows the similar band absorptions at wave number of 1050 cm^{-1} – 950 cm^{-1}, 1653 cm^{-1} – 1637 cm^{-1}, and 3749 cm^{-1} – 3377 cm^{-1}. Band observed at 1050 cm^{-1} – 950 cm^{-1} is a characteristic of asymmetric stretching vibration O-Si-O and Al-O-Al at the cage of zeolite structure, that at 1653 cm^{-1} – 1637 cm^{-1} is an indication of the existence of Bronsted acid on the surface of the solid, and that at 3749 cm^{-1} – 3377 cm^{-1} is a characteristic of stretching vibration –OH on the zeolite surface. The presence of –OH group is a characteristic of hydrated zeolite. By definition, zeolite is a mineral which contains hydrated aluminosilicate crystal that could bind cations of alkaline and earth alkaline groups within its three dimensional structure. The cations could then be interchanged without damaging the zeolite structure (Davis, 1991).

CONCLUSIONS

It could be concluded that a well crystallized A-type zeolite could be synthesized from silica gel and aluminium hydroxide as raw materials at the temperature of 75 ^{o}C or more in conventional hydrothermal condition for five hours. The total time for the synthesis is shortened because the ageing period is not required in this method of synthesis. The crystallization temperature less than 75 ^{o}C in this method does not support the formation of well-crystallized A-type zeolite which confirmed by its infra red spectrum.

REFERENCES

Davis, M. E. 1991. *Zeolite and Molecular Sieves: not Just Ordinary Catalysts*. Chemical Engineering Virginia Polytechnic Institute and State University. Blacksburg Virginia.

Donevska, S., J. Tanevski, and N. Daskalova. 1985. Synthesis of Zeolite A from Silicate Raw Materials and Its Application in Formulations of Detergents. *Zeolites*:579-584.

Dutta, P. K. and D. C. Shieh. 1986. Crystallization of Zeolite A: a Spectroscopic Study. *J. Phys. Chem*. 90:2331-2334.

Hosokawa, H. and K. Oki. 2004. Fine Zeolite Particle. US Patent No.6773693.

Hu, H. C. and T. Y. Lee. 1990. Synthesis Kinetics of Zeolite A. *Ind. Eng. Chem. Res.* 29:749-754.

Kuhl, G. 2001. Source Materials for Zeolite Synthesis *in* Verified Synthesis of Zeoliteic Materials. 2nd rev. H. Robson (ed.). Elsevier Science B.V. Amsterdam.

Milton, R. M. 1959. Molecular Sieve Adsorbents. US Patent No.2882243.

Nur, H. 2001. Direct Synthesis of NaA Zeolite from Rice Husk and Carbonaceous Rice Husk Ash. *Indonesian Journal of Agricultural Sciences*. 1:40-45.

Robson, H. 2001. Safety Considerations for Zeolite Synthesis *in* Verified Synthesis of Zeolitic Materials. 2nd rev. H. Robson (ed.). Elsevier Science B.V. Amsterdam.

Stamboliev, Ch., N. Scpova, K. -H. Bergk, and M. Porsch. 1985. Synthesis of Zeolite A and P from Natural and Waste Materials. *Zeolites*:155-160.

Wuntu, A. D. dan H. D. Tangkuman, 2008, Derajat Kristalisasi Sebagai Fungsi Waktu Ageing dan Waktu Kristalisasi pada Sintesis Zeolit A dengn Radiasi Gelombang Mikro, *Majalah Publikasi Ilmu Kimia Chemistry Progress* (1)1:19-24.

Wuntu, A. D. 2002. Sintesis dan Karakterisasi Aluminosilikat Serupa Zeolit. *Jurnal Ilmiah Sains*. 2:4-7.