Microwave preparation of Li-zeolite directly from alumatrane and silatrane

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Abstract
Li-zeolites were 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. Many types of Li-zeolites were obtained by controlling synthesis parameters. 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 min at 110 °C. With increasing temperature, a higher packing density product was generated. Changing Si/Al loading ratio highly influenced the morphology of the synthesized product. With increasing Al loading, more irregular morphology products were obtained. Changing Li2O/SiO2 ratio, led to changes in the unit cell structure and crystal morphology. Lowering the Li2O/SiO2 ratio to one produced FAU type zeolite at 110 °C for 240 min. 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; Zeolite synthesis; Li-zeolite; ABW; EDI; FAU

1. Introduction

Microwave heating techniques are now widely used in many applications of chemical research including organic/inorganic synthesis due to their fast and energy efficient techniques to avoid competitive reactions in many known processes [1]. By combining hydrothermal crystallization with microwave heating technique, a new synthesis method has been developed, giving smaller and more uniform particles in a shorter time [2,3]. 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 solution [4]. 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 conditions [5].

However, some papers reported that cations do not have a structure-directing role, stabilizing soluble silicate or aluminosilicate anion and void filling during crystallization [4,5]. Alkalinites also influence the gel formation [6] and remarkably contribute to the dissolution step of silicate and aluminate anion in the gel [7]. Because of their effect on pH, they can also change the silicate chemistry, thereby playing a critical role in determining what product is formed [8]. 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 agent [9]. 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 ANA [10]. Moreover, Na2O-SiO2 loading ratio affects the morphology of synthesized product [9,10]. As previously stated, the type of alkali strongly

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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.

2. Experimental

2.1. Materials

Fumed silica (SiO2, surface area: 473.5 m² g⁻¹), average particle size of 0.007 µm) and aluminum hydroxide hydrate (Al(OH)₃, surface area: 50.77 m² g⁻¹), were purchased from Sigma Chemical Co. and used as received. Triethanolamine (TEA, N(CH₂ CH₂ OH)₃), and triisopropanolamine (TIS, N(CH₂ CH₃ OH)₃) were supplied by Carlo Erba Reagenti and Fluka Chemical AG, respectively, and used as received. Ethylene glycol (EG, HOCH₂ CH₂ OH) 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 (CH₃ CN) was obtained from Lab-Scan Co., Ltd. and distilled using standard purification methods prior to use.

2.2. Characterization

Thermal properties and stability were analyzed by differential scanning calorimetry (DSC). DSC was conducted using a Netzsch instrument: DSC200 Cell and TASC 414/3 controller at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Aluminum pans were used in the DSC analysis with sample sizes of 5–10 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⁻¹ 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° s⁻¹ using Cu Kα. The working range of 2θ is 5–90°. SEM micrographs were obtained with a JEOL JEM 2000EX 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. Hydrothermal treatment by microwave heating technique was conducted using a MSP1000, CME Corporation (Spec. 1000 W and 2450 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.

2.3. Precursors 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 solvent [11]. 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 (1.3 Pa) 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 confirmed 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 to 0.125 mol triisopropanolamine [12]. The crude product was washed with dried acetonitrile for three times which ~90% yield product was obtained and characterized using FTIR, TGA, DSC and FAB⁺-MS. The product was named as AITIS.

2.4. Sol–gel process and microwave technique

SiTEA and AITIS were mixed with lithium hydroxide solution at room temperature at a ratio of SiO₂:Al₂O₃:Li₂O:H₂O (where 0.0115 ≤ x ≤ 6.0, 0 ≤ y ≤ 10 and 63 ≤ z ≤ 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 technique. The solution mixtures containing different ratios of SiO₂:Al₂O₃:Li₂O:H₂O 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 did not have any carbon component in the pores or the framework, as confirmed by EDS/SEM and STA.

3. Results and discussion

Gels started to form at the SiO₂:Li₂O of 1:0.01 and the SiO₂:H₂O 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 SiO₂:H₂O ratios of 1:40. SiO₂:Li₂O ratios were varying from 1:0.7 to 1:10. When with at SiO₂:Li₂O ratio was greater than 1:4, base on XRDs 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.
3.1. 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⁻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⁻¹. 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 Fig. 1. 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 synthesis[1]. Moreover, at different microwave heating temperatures, different types of products were obtained as shown in Fig. 1. By XRD matching showed that at low temperature (in range of 70–90 °C), the EDI type zeolite (PDF#00-0742, LiAlSiO₄·H₂O, 16.6 T Å⁻¹) was obtained while at high temperature (greater than 90 °C), the ABW product (PDF#41-0554, Li₄Al₄Si₄O₁₆·4H₂O, 19 T Å⁻¹) 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 Fig. 2(a), while those of ABW were needle like since the growth in y-direction was lesser than that in x–z direction (Fig. 2(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, LiAlSiO₄) at 400 °C, as illustrated in Fig. 3(a). While ABW was thermally stable up to ~300 °C after which it changed to lithium aluminum silicate (Li₂Al₂Si₂O₈, PDF#40-0063) first and then to LiAlSiO₄ (PDF#26-0839) form at 640 °C (Fig. 3(b)). ABW had higher thermal stability than EDI due to the higher Si-content[13].

Fig. 1. Effect of microwave heating temperature on aluminosilicate crystallinity synthesized from 1SiO₂:0.5Al₂O₃:3Li₂O:410H₂O at 3°C/300 min.

Fig. 2. Unit cell structures and crystal morphologies of (a) EDI and (b) ABW products.

Fig. 3. XRD spectra of (a) EDI and (b) ABW products synthesized from 1SiO₂:0.5Al₂O₃:3Li₂O:410H₂O at 90°C/300 min as a function of temperature.
Based on the SEM result, 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 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.

3.2. Effect of Si:Al ratio in the precursors

After fixing the feed ratios at SiO₂ : 3Li₂O : 410H₂O 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 Fig. 4. At Si/Al loading ratios of more than 1, only lithium silicate (PDF#29-0829, Li₂SiO₃) 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. 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.

3.3. Effect of Li₂O concentration

The effect of Li₂O concentration was studied after fixing the loading ratios of the other components at SiO₂ : 0.5Al₂O₃ : 410H₂O with the synthesis temperature and time fixed at 110 °C and 300 min. The Li₂O/SiO₂ ratio varied from 0.7 to 5. Surprisingly, at Li₂O/SiO₂ ratio of 1, the FAU type zeolite (PDF# 09-1380, Li₂Al₂Si₄O₁₂·8H₂O, 12.7 Å) was obtained mixed with LZ-200 (PDF# 09-1380, Li₂Al₂Si₄O₁₂·8H₂O, 12.7 Å). The XRD spectra of the products are given in Fig. 5 and the crystal morphology and unit cell structure of FAU are illustrated in Fig. 6. The Si/Al ratio of synthesized product was ~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 (Fig. 7). Upon further heating the product became amorphous first and then transformed to lithium alumino-silicate (Li₅Al₄Si₄O₁₄) at 1000 °C. At Li₂O/SiO₂ ratio of 2, the mixture of EDI and FAU were found. For Li₂O/SiO₂ ratio equal to 3, only the ABW type spectra of the products are given in Fig. 5 and the crystal morphology and unit cell structure of FAU are illustrated in Fig. 6. The Si/Al ratio of synthesized product was ~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 (Fig. 7). Upon further heating the product became amorphous first and then transformed to lithium alumino-silicate (Li₅Al₄Si₄O₁₄) at 1000 °C. At Li₂O/SiO₂ ratio of 2, the mixture of EDI and FAU were found. For Li₂O/SiO₂ ratio equal to 3, only the ABW type
was found. At LiO\(_2\)/SiO\(_2\) ratio of 4, a mixture of EDI and silicon nitride (PDF#33-1160, Si\(_3\)N\(_4\)) were produced and at Li\(_2\)O/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 Li\(_2\)O/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 (Fig. 8). They show that the Li\(_2\)O concentration had a strong influence on the product type due to the change 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.

3.4. Effect of microwave heating time

By fixing the precursor ratios at SiO\(_2\):0.5Al\(_2\)O\(_3\):3Li\(_2\)O:410H\(_2\)O and the temperature 110\(^\circ\)C, we studied the effect of microwave heating time. Fig. 9 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 (Fig. 2). 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 SEMs results (Fig. 10), most particles have size in range of ~1–1.5 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 Li2O/SiO2 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.

4. Conclusions

Lithium aluminosilicates can be one-step synthesized directly from aluminatrane 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 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, Li2O/SiO2 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. Li2O/SiO2 starting ratio strongly affected the types of zeolite obtained in the products. With increasing Li2O/SiO2 ratio, the structure type changed to higher packing density product. Lowering the Li2O/SiO2 ratio to 1, FAU type zeolite was produced. Fixing the precursor ratios at SiO2:0.5Al2O3:3Li2O:410H2O and microwave heating temperature at 110 °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 °C, only EDI product having lower packing density than ABW was produced.
confirming that at 110°C, the energy provided was too high.

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