

Effect of the TEOS /Al(i-pro)₃ mol ratio in the composition on the crystal morphology of zeolites

Ik Jin Kim^{a,*}, Wei Zhao^a, Xiaou Fan^c, Jeong Ho Chang^b and Ludwig J. Gauckler^c

^aInstitute for Processing and Application of Inorganic Materials (PAIM), Dept. of Materials Science and Engineering, Hanseo University, Seosan 356-706, Korea

^bKorea Institute of Ceramic Engineering and Technology(KICET), 233-5, Gasan-Dong, Guencheon-Gu, Seoul, 153-801, Korea

^cNonmetallic Inorganic Materials, Department of Materials, ETH Zurich, Switzerland

The interest is focused on the control of crystal morphology of single phase zeolite nanocrystals from cube, LTA to octahedron, Faujasite by the mol ratio of TEOS /Al(i-pro)₃ in the mother solution, a Al(i-pro)₃ : 2.2 TEOS: 2.4-5.7 TMAOH: 0.3 NaOH : 200 H₂O compositions. Well- controlled single nanocrystals of a high quality zeolite LTA with a size of 264 nm and sodalite with a size of 30-50 nm were synthesized by the compositions having a TEOS /Al(i-pro)₃ : 2.2 and 5.2, respectively. The synthesized crystals were characterized by scanning electron microscopy (SEM), high resolution transmission electron microscopy(HRTEM), X-ray powder diffraction(XRD), and dynamic light scattering (DLS).

Key words: zeolite, LTA, Faujasite, Sodalite, nanocrystals, morphology, particle size.

Introduction

Zeolite crystals are ordered framework materials with regular cages and channels of sub-nanometre size. Their tailored structure, stability, and activity have led to a broad variety of applications such as a micro reactor for model reaction, chemical sensor and host materials for semiconductor quantum dots [1, 2] In general, quantum dots are semiconductor crystals typically between 1 and 10 nanometres in diameter and have unique properties between that of single molecules and bulk materials. Quantum dots offer tunable optical and electronic properties that can work around natural limits inherent in traditional semiconductors [3, 4].

However, a quantum dot is only useful if it is robust (strong), stable and long lasting. Therefore, we need perfected coatings and surfaces of host materials to make quantum dots more durable with better performance. The success in the application of zeolites as advanced host materials of the current worldwide emphasis on nanotechnology is the acquisition of the ability to assemble nanoparticles into highly ordered and oriented bulk structures. Most of the nanocrystals that have been employed for forming a self-assembled monolayer or multilayer films or bulk structures are spherical. Since spheres are symmetric in every respect, they naturally have a strong tendency to closely pack and the resulting well-packed bulk structures usually show a high ordering of nanospheres throughout

the assembled structures [5, 6]. However, most morphologies of zeolite crystals are nonspherical, for example, cubic zeolite A or octahedral zeolite-X, and -Y, the nanocrystals are likely to orient randomly within the self-assembled bulk structures, and at this stage there are no methods available to uniformly orient or align them within the 3-D structures. Therefore, acquiring the ability to control orientation or alignment of the nanoparticles within the resulting 3-D structures is highly challenging and crucial for the development of nanotechnology [7, 8]. Zeolite crystals which are well morphologically controlled and of a high quality are very important for a variety of studies, such as a fundamental understanding for the crystallization process including nucleation, crystal growth, and phase transformations, such as in applications based on short diffusion times of molecules in their voids (channels or cages) and with their large surface to internal surface area and for surface reactivity for retreatment such as the re-growth of larger crystals or thin films [9, 10].

In this study, zeolite nanocrystals are synthesized by a hydrothermal method at a predetermined elevated temperature from pure aqueous synthesis solutions containing an alumina source, a silica source and an alkali source. The SiO₂/Al₂O₃ ratio, water content, reaction temperature and time determine which type of zeolite crystal will form, as well as its properties such as the crystal size and morphology [11]. The main interest of this study is to focus on investigating the morphological control by changing the TEOS/Al (i-pro)₃ ratio in the synthetic gel and the effects of reaction parameters, which includes reaction temperature (pressure), reaction time and water content on the crystal size and morphology from cubic,

*Corresponding author:
Tel : +82-41-660-1441
Fax: +82-41-688-4143
E-mail: ijkim@hanseo.ac.kr

LTA (Linde Type A) Zeolite, to octahedral, Faujasite (NaX and NaY) and to sodalite, respectively.

Experimental Procedure

Zeolite nanocrystals of a uniform particle size of 264 nm for LTA and 30 nm for sodalite were synthesized by a hydrothermal method in a mother solution having compositions of Al(i-pro)₃ : 2.2-5.2 TEOS: 2.4-5.7 TMAOH: 0.3 NaOH : 200-400 H₂O compositions at 90, 100, and 110 for 3 ~7 days. Table 1 gives the chemical compositions for zeolite synthesis under different conditions. The reactant materials used were aluminium isopropoxide Al(i-pro)₃ (Aldrich, 98 wt%), tetraethylorthosilicate (TEOS, Aldrich, 98 wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25 wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99 wt%).

In order to investigate the impact of the TEOS/Al(i-pro)₃ ratio on the morphology of synthesized zeolite nanocrystals, four different mother solutions were produced, with a TEOS/Al(i-pro)₃ ratio of 2.2(R1), 3.2(R2), 4.2(R3) and 5.2(R4). All other reaction parameters were kept constant for the synthesis process accomplished with the first three mother solutions (R1, R2 and R3). The reaction temperature was fixed at 100 °C, the reaction time was 3 days, and the Al(i-pro)₃/water mol ratio in the mother solution was always 1 : 200. The crystallization in the mother solution with a TEOS/Al(i-pro)₃ ratio of 5.2 (R4) required a higher temperature and longer reaction time, therefore the synthesis process was carried out at 110 °C for 5, 7 and 10 days.

Fig. 1 shows the typical experimental procedure for zeolite synthesis. The first part of the synthesis of the mother solution called solution 1 was prepared by adding TMAOH to a Al(i-pro)₃ solution, which was stirred at room temperature for one hour. The solution was stirred at room temperature (RT) for one hour and subsequently filtrated with 0.2 µm membrane filter in order to remove impurities and get a homogenous particle distribution. The second part of the synthesis of the mother solution called solution 2 was prepared by drop by drop adding TEOS to the NaOH solution, which has been stirred at RT for two hours and already filtered with the same membrane filter as before. Afterwards, the two synthesis mixtures were mixed together, and aged for 24 hours at RT. Finally, the synthesis mother solution was loaded to a 250 ml Teflon autoclave. Crystallization was carried

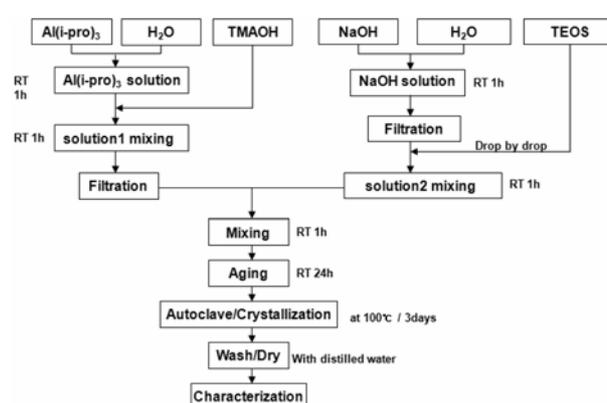


Fig. 1. Schematic experimental procedure for zeolite synthesis.

out at predetermined temperatures and times. At the end, the autoclave was removed from the oven to arrest the reaction. The crystallized samples were collected and separated by centrifugation. The products were repeatedly dispersed in distilled water using ultra sonication and centrifugation as above to remove the remaining mother solution until the pH of the dispersion was close to 7. The samples were obtained by drying at 50 °C for 24 h.

The nanoparticles were characterized by X-ray diffraction (XRD, Model RAD-2B, Rigaku Co.) with CuK α radiation, scanning electron microscopy (SEM, XL-30, FEG), high resolution transmission electron microscopy (HRTEM, Tecnai G2, STEM), and dynamic light scattering (DLS) analysis. A semiquantitative chemical analysis performed to estimate the SiO₂/Al₂O₃ ratio by fluorescent X-ray spectrometry (Model 3070, Rigaku Co., Tokyo, Japan).

Results and Discussion

SEM and TEM

Fig. 2(a) shows the SEM image of synthesized zeolite crystals with the R1 mother solution. The crystals have a typical cubic form from the LTA zeolite with an average edge size of ca. 165 nm in-edge, which was determined by DLS. The corresponding TEM image (Fig. 3(a)) shows both high crystallinity and perfect crystal morphology. Fig. 2(b) shows the SEM image of synthesized zeolite crystals with the R2 mother solution. Two different kinds of crystals are present in this image. One has a typical cubic form with an average edge size of ca. 200 nm, another one has an unclear form with an average edge size of ca. 50 nm. The crystals connect with each other;

Table 1. The Chemical Compositions for Zeolite Synthesis under Different Conditions

Materials	TMAOH [mol]	Al(i-pro) ₃ [mol]	TEOS [mol]	NaOH [mol]	H ₂ O [mol]	Reaction temp.[°C]/time[days]
R1	2.40	1.0	2.2	0.3	200	90/3
					400	100/1, 2, 3
					600	110/3
R2	3.50	1.0	3.2	0.3	200	100/3
R3	4.59	1.0	4.2	0.3	200	100/3
R4	5.70	1.0	5.2	0.3	200	100/5, 7, 10

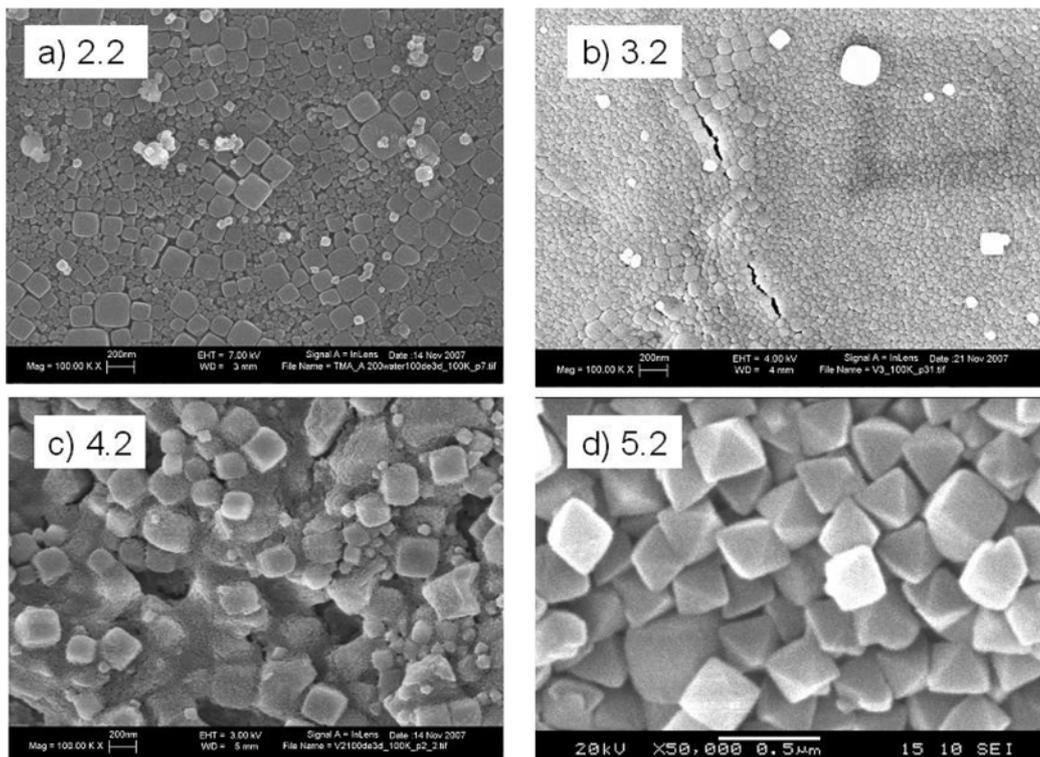


Fig. 2. SEM images of zeolite crystals as a function of mol ratio of TEOS/ Al(i-pro)₃.

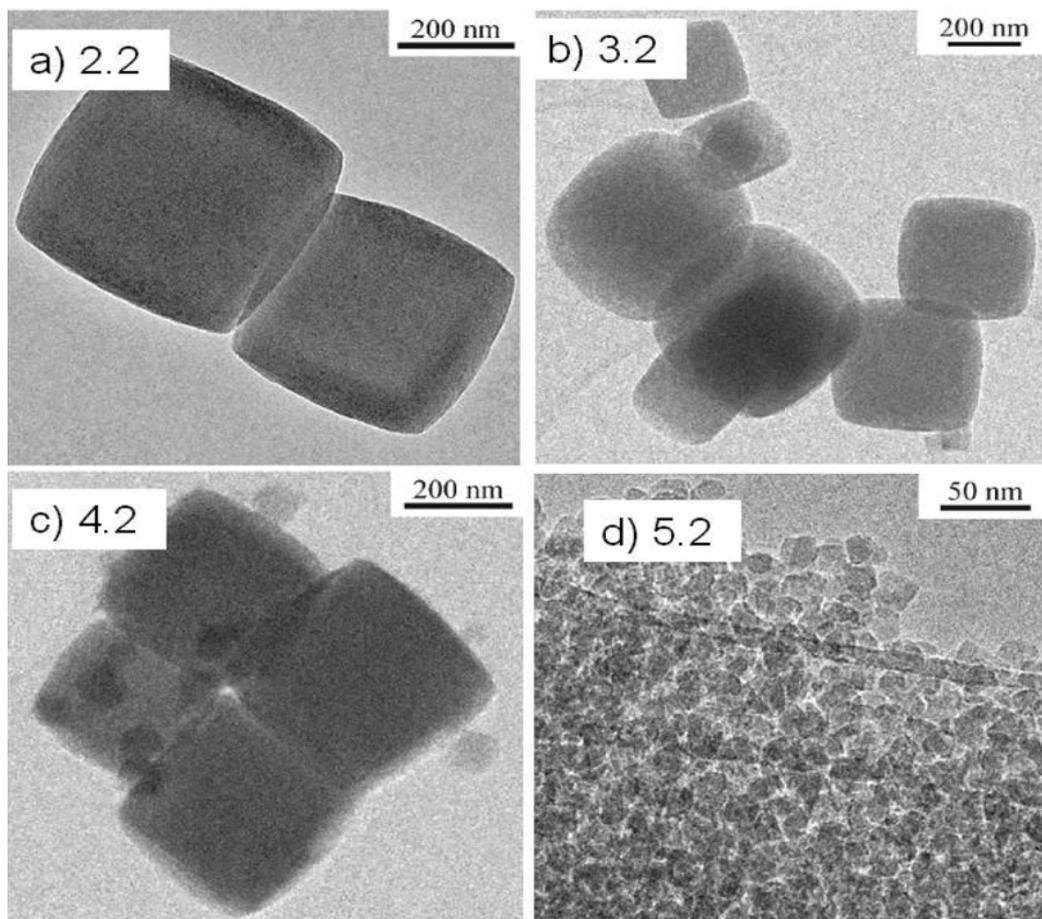


Fig. 3. HRTEM images of synthesized zeolite as a function of mol ratio of TEOS/ Al(i-pro)₃.

there is no visible gap between them. The corresponding TEM image (Fig. 3(b)) confirms the existence of two different types of zeolite, namely LTA and NaY crystals.

Fig. 2(c) shows the SEM image of synthesized zeolite crystals with the R3 mother solution. Again, two different kinds of crystals are present in this image. One of them has a typical cubic form with a average edge size of ca. 250 nm, namely LTA crystals. Another one has an Octahydro form with an average size of ca. 50 nm, namely NaY crystals. More NaY crystals are synthesized with the R3 mother solution than with the R2. The corresponding TEM image (Fig. 3(c)) also confirms the existence of LTA and NaY zeolite crystals. Fig. 2(d) shows the SEM image of synthesized zeolite crystals with the R4 mother solution. The synthesized crystals have a typical Octahydrate form with an average edge size of ca. 30 nm. The sample has an almost uniform crystal size. The corresponding TEM image (Fig. 3(d)) shows both high crystallinity and perfect crystal morphology.

XRD patterns of synthesized Zeolite crystals

Crystallization from solution usually occurs via the sequential steps of nucleation of the phase, dictated by the composition of the solution, followed by growth of the nuclei to large sizes by incorporation of materials from the solution [11]. Furthermore, the use of pure reactant sources can increase the homogenous distribution of the crystal size by reducing the number of heteronuclei and favor the formation of single phase crystals. The ratios of TEOS/Al(i-pro)₃ all have an essential influence on the final crystal size and morphology of zeolites. Fig. 4 shows powder X-ray diffraction patterns of synthesized zeolite nanocrystals in the 3 different mother solutions (R1, R2 and R3). The XRD peaks correspond to zeolite in the form of either LTA or mixed LTA-FAU crystals. The nanocrystals synthesized with R1 are relatively high purity LTA (Pm3m, a = 12.157 Å) crystals with 5% contamination of NaY zeolite, which is indicated at $2\theta = 6.0^\circ$. The nanocrystals synthesized with R2 and R3 are mixed NaA and NaY (Fd-3m, a = 24.868 Å) crystals. The characteristic peak of the NaY crystals at $2\theta = 6.3^\circ$ from nanocrystals synthesized with R3 is more intensive than the one from nanocrystals synthesized with R2.

It can be seen from Figs. 4 and 5 that increasing the TEOS /Al(i-pro)₃ ratio results in a change of the crystals from cubic, LTA to octahedral, Faujasite (NaY), and sodalite and a change in the crystal morphology from cube, cube + octahedron to octahedron with decreasing crystal sizes. But further increasing the TEOS /Al(i-pro)₃ ratio to above 5.2 shows the formation of the pure phase of sodalite which is disordered crystal form. The morphology of the LTA zeolite crystals from the electron microscope images shows that a cube is comprised of well-controlled crystals between 164 and 264 nm in size in a configuration having six planes as shown in Fig. 3. Fig. 5 shows X-ray diffraction patterns of synthesized zeolite nanocrystals with R4 at 110 °C for 5, 7 and 10 days. The XRD peaks

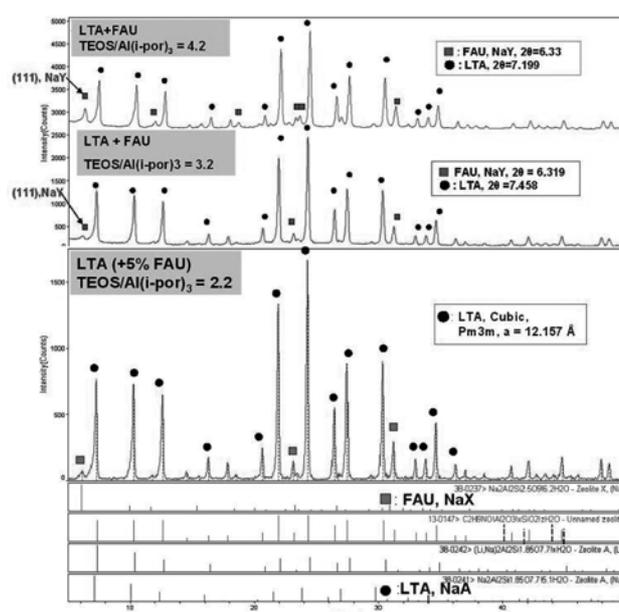


Fig. 4. X-ray diffraction pattern of synthesized TMA-A nanocrystals at 100 °C for 3 days.

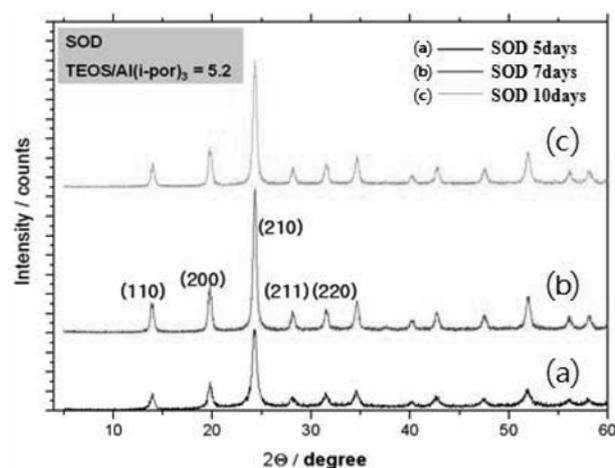


Fig. 5. X-ray diffraction pattern of synthesized nanocrystals with the R4 mother solution at 110 °C for 5, 7 and 10 days.

are characteristic of Sodalite Octahydrate crystals (Im3m, a = 8.975 Å) which is a disordered crystal form [12]. The nanocrystals synthesized with R4 at 110 °C for 7 days have the highest crystallinity, whereas the ones synthesized with R4 at 110 °C for 5 days have a relatively lower crystallinity. Table 2 shows zeolite crystals synthesized with different mol ratios of TEOS /Al(i-pro)₃.

Effects of Reaction Parameters

Reaction temperature and water content

Nucleation and crystallization typically are governed by a driving force related to the supersaturation and reaction temperature under the autogenous pressure. The characteristic crystallization curve of a zeolite has a S-shape, and can be divided into three periods. Part I is the "induction period", during which crystalline nuclei form but no

Table 2. The Products Synthesized with Four Different Mother Solutions

TEOS/Al (i-pro) ₃	Framework type	Material	Canvic str Lattice constant	Crystal Morpology	Pore Dimension	Particle size by TEM
2.2	LTA	NaA NaX, (5%)	Pm3m a = 12.157 Å	Cube Octahedron	4 Å	264 nm [164.8]
3.2	LTA + FAU	NaA + NaY, (5%)	Pm3m a = 12.157 Å Fd-3m a = 24. Å	Cube + Octahedron	4 Å + 7~8 Å	200~400 nm [130]
4.2	LTA + FAU	NaA + NaY	Pm3m a = 12.157 Å Fd-3m a = 24. Å	Cube + Octahedron	4 Å + 7~8 Å	150~30 nm [100]
5.2	SOD	Sodalite Octahydrate, 100%	Pm3m a = 8.975 Å	Octahedron	Space filling Structure	30~50 nm [54.8]

● [] : particle size tested by DLS

crystalline product is observed by XRD. The length of the induction period is reduced with a higher reaction temperature and lower H₂O concentration in the gel. During the growth period, II, crystal nuclei grow rapidly in size. Finally, during period III the crystallization is over after a certain number of days [13]. The reaction temperature influences zeolite nucleation in the aluminosilicate gel. Zeolite nucleation from aluminosilicate gels is well known to increase with increasing temperature and increasing alkali concentration in the gel.

Fig. 6 and 7 represent the particle size distributions of synthesized zeolite crystals as a function of reaction temperature and water content. The higher the temperature or the alkali concentration in the gel, the larger is the average particle size. At 90 °C and 100 °C synthesized crystals have a narrow size distribution, whereas at 110 °C synthesized crystals have a bimodal size distribution. Zeolite crystals synthesized with high an alkali concentration (200 mol water) have a biomodal size distribution, whereas the biomodal size distribution is not visible for the crystals

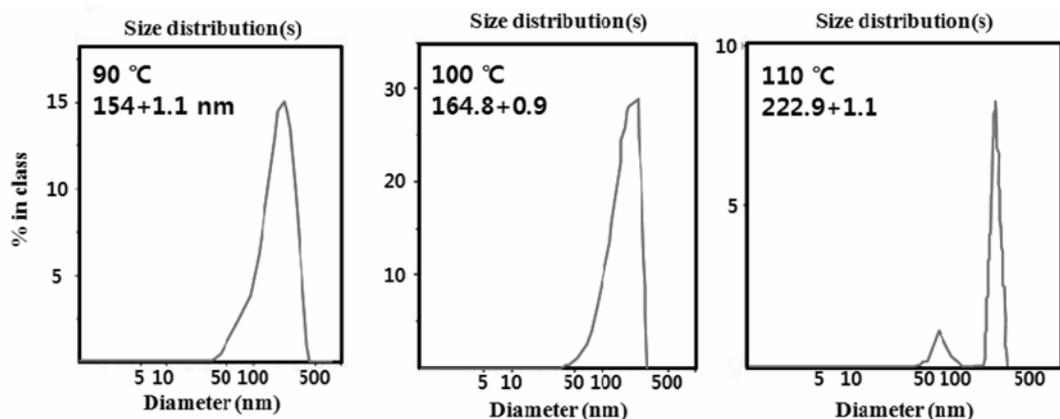


Fig. 6. Particle size distribution of zeolite (R1) as a function of reaction temperature (90, 100, and 110 °C) for 3 days.

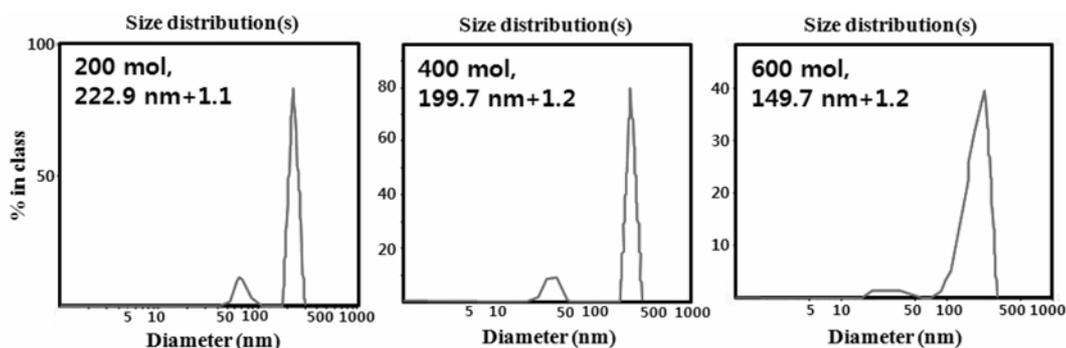


Fig. 7. Particle size distribution of zeolite (R1) as a function of water content (200, 400 and 600 mol) in the mother solution at 100 °C for 3 days.

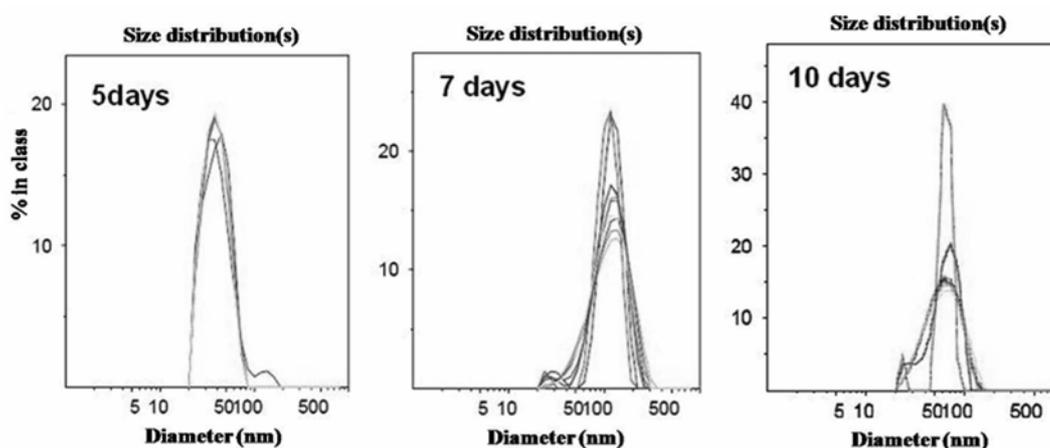


Fig. 8. Particle size distribution of synthesized SOD Zeolite (R4) as a function of reaction time (5, 7 and 10 days) at 110 °C.

synthesized with a lower alkali concentration (600 mol water). With decreasing crystallization temperature or a decrease in the alkali concentration in the gel, the particle size distribution becomes narrower.

Reaction time

With an increase in the reaction time, higher crystallinity and larger average crystal size are to be expected. Fig. 8 shows the particle size distribution of synthesized SOD Zeolite as a function of reaction time (5, 7 and 10 days) at 110 °C. The crystals synthesized for 5 days have a narrow particle distribution, whereas the crystals synthesized for 7 and 10 days at 110 °C sometimes display a bimodal distribution.

Conclusions

The main objective of this research, as outlined in the introduction, was to investigate the morphological control by changing the TEOS/Al(i-pro)₃ ratio in a synthetic gel and to investigate the effects of reaction parameters on the crystal size and morphology, which includes reaction temperature (pressure), reaction time and water content (alkali concentration). Well-controlled single nanocrystals of high quality zeolite LTA with a size of 264 nm, faujasite with a size of 100–150 nm and sodalite with a size of 30–50 nm were synthesized from the compositions having a TEOS/Al(i-pro)₃ : 2.2 and 5.2, respectively. If the TEOS/Al(i-pro)₃ ratio is equal to 2.2, highly pure LTA zeolite crystals are synthesized, which present a typical cubic form. If the TEOS/Al(i-pro)₃ ratio is equal to 3.2 or 4.2, mixed LTA and faujasite (above 90%) zeolite crystals are produced, which present either a cubic or an octahedral form. If the TEOS/Al(i-pro)₃ ratio is equal to 5.2, highly pure SOD zeolite crystals are produced, which display an octahedral morphology. With decreasing crystallization

temperature or a decrease in the alkali concentration in the gel, the particle size distribution becomes narrower.

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