Influence of Synthesis Parameters on the Morphology and Particle Size Distribution of Zeolite L

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Abstract: Zeolite L was synthesized hydrothermally from the substrate mixture of Na₂O-K₂O-Al₂O₃-SiO₂-H₂O system at temperatures of 373 – 443 K, and the influence of various synthesis parameters on the particle size distribution and surface morphology was investigated. The crystalline zeolite L samples obtained were characterized by means of X-ray powder diffraction, scanning electron microscopy, and particle size analysis. It was established that as the synthesis temperature increased, the average crystal size becomes larger with a broader particle size distribution. Particle size distribution and morphology of zeolite L was also affected by the silica source and the molar ratios of SiO₂/Al₂O₃, (K₂O + Na₂O)/SiO₂, Na₂O/(K₂O + Na₂O), and H₂O/(K₂O + Na₂O). The crystal size decreased significantly by stirring the gel during the synthesis or subjecting the substrate mixture to an aging treatment at room temperature before hydrothermal treatment. Different heating rates applied prior to subsequent isothermal crystallization at 443 K also significantly influence the particle size distribution and the morphology of zeolite L.

Keywords: zeolite L, synthesis, particle size distribution, morphology, stirring, heating rate

Introduction

Zeolite L has one-dimensional pores of about 0.71 nm aperture leading to cavities of about 0.48 × 1.24 × 1.07 nm; its Si/Al ratio is typically 3.0 [1-3]. Because of its unique structural features, zeolite L is known as a good support for noble metal catalysts used in aromatization of C₆-hydrocarbons of normal structure and is being used commercially in the Chevron Aromax cyclization process [4]. The properties of L-type zeolite with regards to its structure [1,3], adsorptive properties [5,6], and catalytic properties [7] have been investigated earlier. The preparation of zeolite L has been reported mostly in patents [8-12]. According to Wortel [11], zeolite L having a cylindrical morphology comprised of crystallites with a mean diameter of at least 0.1 micron, preferably at least 0.5, is particularly valuable for use as a catalyst support in hydrocarbon conversion. Vaughan [12] reported a process for preparing zeolite L using organic templates, the most preferable one being the tetraethylammonium cation. Verdijin [13,14] reported that zeolite L was prepared with flat basal planes and a smaller crystallite size from the synthesis gel modified by the addition of small amounts of additional metals. Joshi and coworkers [15] reported the effects of substrate composition on the crystallization kinetics of zeolite L, and Meng and coworkers [16] synthesized an ultrafine zeolite L with a crystal diameter of ~0.30 nm. Isomorphous substitution of Fe³⁺ for Al³⁺ in the zeolite L framework has been reported by us recently [17].

Although a considerable amount of information is available in the literature describing various synthetic routes and crystallization kinetics of zeolite L, no studies dealing with particle size distribution and morphology of zeolite L have been reported so far. In this study, the effects of the raw starting materials, substrate composition, reaction temperature, reaction time, gel aging, stirring, and heating rate upon the particle size and distribution of zeolite L have been evaluated systematically.

Experimental

Zeolite L synthesis was conducted from the substrates
having the following composition ranges expressed as oxide mole ratios: SiO₂/Al₂O₃ = 10 ~ 35, (K₂O+Na₂O)/
SiO₂ = 0.30 ~ 0.55, Na₂O(K₂O+Na₂O) = 0.20 ~ 0.68, H₂O/
(K₂O+Na₂O) = 30 ~ 60. In preparing the substrates for
hydrothermal synthesis, colloidal silica sol (Ludox HS-40
from DuPont, 40% SiO₂), Zeosil 77 fine silica powder
(KoFran Co., 91.8% SiO₂), and aqueous sodium silicate
solution (KoFran Co., 25.3% SiO₂, 6.6% Na₂O) were
used as silica sources, and sodium aluminate (Junsei Co.,
32.6% Na₂O, 35.7% Al₂O₃) was used for alumina. Pot-
sassium hydroxide (Tedia Co., 85%) and sodium hydroxide
(Tedia Co., 98%) were used as the sources of the alkali
metal cations.

Sodium hydroxide, potassium hydroxide, and alumina
source were added to deionized water in a Teflon vessel
(100 mL) and stirred until the alumina source had com-
pletely dissolved. This solution was then added slowly to
the aqueous silica solution and the whole mixture was
stirred vigorously for a further 30 min for homogenization.
The reaction mixture was transferred to a series of 100
mL Teflon-lined stainless-steel vessels and kept in a
convection oven maintained at 373 ~ 443 K. In some
cases, crystallization was also performed while stirring
using a magnetic bar or conducting an aging treatment at
room temperature prior to the hydrothermal reaction.
Reaction vessels were removed from the oven at the
scheduled time intervals and were quenched immediately
in cold water. The solid products were separated by
filtration and washed with deionized water repeatedly
until the pH of the washed liquid was 9. Finally, the
products were dried in an oven at 393 K for 12 h before
characterization.

The samples were analyzed by X-ray diffraction (XRD)
for phase identification. The unit used was a powder
X-ray diffractometer (Phillips, PW-1700) with a scintilla-
counter and a graphite monochromator attachment,
utilizing Ni-filtered CuK radiation. To calculate crystal-
linity, peaks located at 2θ = 5.5, 19.4, 22.7, 28.0, 29.1,
and 30.7 were used to avoid possible interference of the
coeexisting phases, such as zeolites W or T, for a given
sample. The pure sample having the most-intense peaks
was taken as a reference (assigned 100% crystallinity),
and the percentage crystallinity of the other samples was
calculated relative to the reference. The morphology of
the crystalline phase was examined using a scanning
electron microscope (Hitachi, X-650) after coating with
an Au-Pd evaporated film. The average crystal size and
particle size distribution were measured using a dynamic
light scattering particle size analyzer (Malvern, Zetasizer
4), which employs the PCS (Photon correlation spectro-
copy) principle based on the Brownian motion of the
particiles and set with a maximum beam intensity of 10.5
for the particles of the highest abundance. The upper
and lower particle sizes to be scanned were set automatically

![XRD and FT-IR spectra](image)

**Figure 1.** (a) XRD and (b) FT-IR spectroscopic patterns of
zeolite L obtained at 443 K after 24 h.

based on the maximum beam intensity, and the scan
range was divided into 24 sections between the limits. To
avoid counting amorphous gel particles, the gel was
treated in 1.5 M NaOH solution for half an hour. Mor-
phology and particle size distribution were examined
using powder samples of zeolite L not contaminated with
other crystalline phases.

### Results and Discussion

Figure 1 shows the X-ray diffraction pattern and FT-IR
spectrum of zeolite L crystals obtained after hydro-
thermal reaction for 24 h at 443 K from a substrate com-
position of 5.4K₂O-5.7Na₂O·Al₂O₃·30SiO₂·500H₂O. Unless
otherwise stated, Ludox HS-40 was used as the silica
source. Characteristic XRD peaks corresponding to highly
crystalline zeolite L crystals were obtained for a given set
of synthesis conditions; the IR spectrum agrees closely
with that reported in the literature [18]. Joshi and coworkers [15] observed that zeolite T was obtained on prolonged hydrothermal treatment in the K/Na mixed cation system. However, no other crystalline phases were detected in the XRD pattern of this sample, even after the prolonged crystallization up to 72 h.

Figure 2 shows the particle size distribution curves of zeolite L samples prepared with different crystallization times at 443 K. The average crystal sizes after crystallization periods of 12, 20, and 24 h were 0.24, 1.16, and 1.46 \( \mu m \), respectively, and the particle size distribution gradually became broader as the crystals grow in time.

Figure 3 shows the particle size distribution curves of zeolite L samples obtained at different reaction temperatures. Particle size distribution was measured at each synthesis temperature after the maximum crystallinity was obtained, and the time taken to reach the maximum in each case is denoted in the legend in Figure 3. Under a given set of substrate compositions, both the rate of nucleation and crystal growth at high temperature were much faster than those at low temperature, and as the reaction temperature increased to 373, 403, 423, and 443 K, the average crystal size increased from 0.57 to 0.92, 1.10, and 2.97 \( \mu m \), respectively, and the particle size distribution gradually became broader.

The initial composition of a given substrate mixture is very important in determining the zeolite types to be crystallized and, especially, the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio is the critical factor for the zeolite phase obtained and its yields [19]. Figure 4 shows the particle size distribution curves of zeolite L samples obtained with different \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratios at constant (\( \text{K}_2\text{O}+\text{Na}_2\text{O} \))/(\( \text{SiO}_2 \)), \( \text{Na}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O}) \), and \( \text{H}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O}) \). The higher the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio, the larger the zeolite L crystals; the samples with \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratios of 28, 30, and 33 had average crystal sizes of 0.84, 1.46, and 2.24 \( \mu m \), respectively. The particle size distribution gradually became broader upon increasing the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio and a substantially narrow crystal size distribution was obtained at a \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio of 28. The
shapes of the zeolite L crystals were also affected by the SiO$_2$/Al$_2$O$_3$ ratio of the synthesis mixture. Most of the crystals were produced as a typical clam-shaped crystals of a domed basal plane, whereas the highly siliceous gel at a SiO$_2$/Al$_2$O$_3$ ratio of 33 produced crystals having basal planes of more flatness.

A change in alkali concentration in the synthesis mixture may cause a change in the rate of nucleation and so does the presence of hydroxide ions, which strongly affects the formation of nuclei. When solutions of the aluminophosphate anions are mixed to form the hydrogels, a strong base, such as NaOH, or KOH, accelerates the dissolution of the gel. The dissolved silicate and aluminate ions undergo a polymerization process to form aluminosilicate or polysilicate ions, and the soluble aluminosilicate or polysilicate species subsequently regroup around the hydrated anion to form the nuclei of the ordered zeolite. Figure 5 shows the SEM photographs of the zeolite L samples with various (K$_2$O+Na$_2$O)/SiO$_2$ ratios at constant SiO$_2$/Al$_2$O$_3$, Na$_2$O/(K$_2$O+Na$_2$O), and H$_2$O/(K$_2$O+Na$_2$O) ratios. The morphology appears to be sensitive to the (K$_2$O+Na$_2$O)/SiO$_2$ ratio of the synthesis mixture. A distinctive characteristic in the morphology was the formation of ice-hockey-puck-shaped crystals at the (K$_2$O+Na$_2$O)/SiO$_2$ ratio of 0.37 as in Figure 5(b) accompanied by a decrease in crystal size as the (K$_2$O+Na$_2$O)/SiO$_2$ ratios increased. Verduijn [20] demonstrated that a Pt-loaded zeolite L catalyst with ice-hockey puck morphology showed significantly improved selectivity and stability over that of a typical clam-shaped zeolite L for the aromatization of light aliphatic hydrocarbons.

Figure 6 shows the particle size distribution curves of zeolite L samples obtained with different (K$_2$O+Na$_2$O)/SiO$_2$ ratios. The samples with (K$_2$O+Na$_2$O)/SiO$_2$ ratios of 0.37, 0.40, and 0.43 had average crystal sizes of 0.95, 0.72, and 0.42 $\mu$m, respectively, and the zeolite L samples obtained at higher (K$_2$O+Na$_2$O)/SiO$_2$ ratios showed narrower ranges of the particle size distributions as well as smaller average sizes due to the enhanced mineralization at a high concentration of alkali.

The H$_2$O/(K$_2$O+Na$_2$O) ratio in the synthesis mixture also influenced the crystal size and shape of zeolite L samples synthesized at 443 K for 24 h. Figure 7 shows the particle size distribution curves of zeolite L samples obtained with different H$_2$O/(K$_2$O+Na$_2$O) ratios at constant
SiO₂/Al₂O₃, (K₂O+Na₂O)/SiO₂, and Na₂O/(K₂O+Na₂O) ratios. The average crystal size of zeolite L became larger as the concentration of the combined alkali decreases as a result of an increase of water content in the synthesis mixture. It can be conjectured that this finding is a consequence of facile diffusion or interaction of the reaction components with decreasing viscosity of the aluminosilicate gel; the initial crystallites assemble in the reaction medium with relatively high concentration of synthesis components. However, formation of the second group of crystallites from collision assembling of the initially generated crystallites or their growth can be facilitated at a lower substrate concentration. The particle size distribution gradually became broader as the H₂O/(K₂O+Na₂O) ratio increased up to 48, but this trend was interrupted suddenly at the H₂O/(K₂O+Na₂O) ratio of 50, which showed significantly narrower particle size distribution with the appearance of the ice-hockey-puck-shaped crystals. Repeated experiments produced much the same result. Whilst no clear explanation can be offered at this stage, it seems that the water content in the synthesis mixture has a strong influence on the morphology of zeolite L crystals and, concurrently, their particle size distribution.

Cations in the synthesis mixture often are the dominant factor determining which zeolite structure is formed. The influence of replacing K⁺, by Na⁺, and vice versa, on the crystallization kinetics, crystalline phase purity, and crystal morphology has been reported [21,22]. With only a small change in the cation content of the synthesis mixture, completely different zeolite products may be formed. The crystallinity of a particular desired zeolite phase can also be improved by the choice and amount of inorganic cation used in the synthesis gel. It is known that K⁺ ions are necessary for the crystallization of pure zeolite L, because its framework structure is based on the cancrinite cage occupied by K⁺ ion [23]. However, the crystallinity of zeolite L can be improved by the addition of sodium ions to the synthesis gel. The sodium replacement of potassium ions, which is given by the ratio Na₂O/(K₂O+Na₂O) in the reaction mixture under the
same SiO$_2$/Al$_2$O$_3$, (K$_2$O+Na$_2$O)/SiO$_2$, and H$_2$O/(K$_2$O+Na$_2$O) ratios, was found to affect both the degree of crystallization and the morphology of the product crystals. Figure 8 shows the particle size distribution curves of zeolite L samples obtained with different Na$_2$O/(K$_2$O+Na$_2$O) ratios at constant SiO$_2$/Al$_2$O$_3$, (K$_2$O+Na$_2$O)/SiNa$_2$O/ (K$_2$O+Na$_2$O) ratios O$_2$, and H$_2$O/(K$_2$O+Na$_2$O) ratios. As the Na$_2$O/(K$_2$O+Na$_2$O) ratio increased to 0.4, 0.5, and 0.55, average crystal size gradually decreased to 2.89, 1.20, and 0.62 μm, respectively, and the particle size distribution became narrower. Apparently, the increase in the Na$_2$O/(K$_2$O+Na$_2$O) ratio in the synthesis mixture led to an increase in the number of nuclei, leading to zeolite crystals of a smaller average size. The zeolite L crystals obtained at Na$_2$O/(K$_2$O+Na$_2$O) ratios of 0.5–0.55 had very uniform crystal size distributions. Regardless of the Na$_2$O/(K$_2$O+Na$_2$O) ratio, all of the zeolite L samples synthesized had clam-shaped crystals.

Figure 9 shows the particle size distribution curves of the zeolite L samples obtained using different silica sources. The zeolite L samples obtained with Ludox HS-40, Zeosil, and sodium silicate solution made-up with Zeosil to match the substrate composition of the three samples, have average crystal sizes of 1.46, 0.39, and 0.41 μm, respectively; the particle size distribution became narrower in the order of sodium silicate solution made-up with Zeosil, Zeosil, and Ludox HS-40. In particular, the crystals of zeolite L formed using sodium silicate solution made-up with Zeosil had the highest degree of uniformity in particle size.

Figure 10 shows the particle size distribution of zeolite L samples synthesized from the gel aged for 1 day using Ludox and Zeosil as silica sources. L samples synthesized from the gel aged for 1 day using Ludox or Zeosil as the silica source under static conditions. For both of the silica sources, aging of the initial gel prior to crystallization led to a decrease in the average crystal size of zeolite L. We believe that the aging treatment offers the time required to achieve the formation of nuclei upon dissolution of the silica sources, leading to smaller crystals after hydrothermal reaction. For both silica sources, the particle size distribution became narrower with aging treatment and this effect was more pronounced when Ludox was used as the silica source. Apparently, aging of the synthesis gels can be used effectively not only to reduce crystallization time but also to induce uniformity in the dimensions of the zeolite L crystals.

Usually, stirring a gel during crystallization results in a decrease in the size of the zeolite particles. However, stirring can also change the zeolite structure [24]. Figure 11 shows the particle size distribution curves of zeolite L samples obtained under static or stirred condition. The crystals of zeolite L formed under stirring were smaller in average crystal size and narrower in size distribution than those produced under static conditions. However, when both aging treatment and stirring were applied at the same time, the crystal dimension was not decreased further than that which resulted from stirring alone. This finding is probably a consequence of the enhanced dis-
solution of the nuclei formed during the aging period upon stirring.

The heating rate may also influence the crystallization of zeolite L. In this study, the heating rate was varied in the range 10~100 K/h using an external heating band controlled by a temperature programmer. The temperature of reaction mixture in a synthesis vessel was elevated from room temperature to 443 K with a constant heating rate with or without stirring and was maintained at this temperature for 24 h. An appreciable effect on the morphology of the zeolite L crystals was observed upon increasing the heating rate. Figure 12 shows the SEM photographs of the zeolite L samples obtained with different heating rates and with or without stirring. As the heating rate was increased, the crystal size of all the samples gradually became somewhat larger, and the crystals showed basal planes of increasing flatness and became more ice-hockey-puck-shaped. In particular, at a heating rate of 100 k/h under static conditions, the zeolite L crystals are the largest and obvious ice-hockey puck or cylindrical-shaped morphologies were obtained. On the other hand, the zeolite L crystals prepared at a constant heating rate of 100 K/h under stirring had an oval-shaped morphology. Figure 13 shows the particle size distribution

![Figure 11. Particle size distribution of zeolite L synthesized without or with stirring at 443 K.](image)

![Figure 12. SEM photographs of zeolite L crystals obtained with different heating rates under static (a, b) or stirring (c, d) conditions. (a) 50 K/h, (b) 100 K/h, (c) 50 K/h, and (d) 100 K/h.](image)
curves of zeolite L samples obtained with different heating rates under static conditions. The particle size distribution gradually became narrower with increased heating rate and this effect was more pronounced at the heating rate of 100 K/h. The effect of the heating rate of the synthesis mixture on the crystallization rate, the morphology, and the particle size distribution of zeolite L in the final products may be accounted for by the dependence of the nucleation rate of a synthesis gel on the heating rates; the sharp increase in crystallization rate of zeolite L upon increasing the heating rate may be connected to the enhancement of the uniform gel nucleation rate, which produced zeolite L crystals with a narrow size distribution.

Conclusions

A systematic study has been undertaken to investigate the effects of various synthesis parameters on the particle size distribution and crystal morphology of zeolite L powders. Investigations revealed that the particle size distribution and morphology of zeolite L depend on the synthetic temperature and molar ratios of the substrate components, such as SiO$_2$/Al$_2$O$_3$, (K$_2$O + Na$_2$O)/SiO$_2$, Na$_2$O/(K$_2$O + Na$_2$O), and H$_2$O/(K$_2$O + Na$_2$O). Crystallization conditions such as aging of the synthesis gel and the stirring and heating rates, also greatly influence the particle size distribution and the morphology of zeolite L crystals. The precursors of the zeolite formed during the aging step, and aging treatment at room temperature before heating the gel produced smaller crystals. Similarly, stirring the gel during crystallization also reduced the particle dimensions and narrowed the size distribution relative to those produced under static conditions. Increasing the heating rate to 443 K before subsequent isothermal crystallization was very effective not only for rapid crystallization but also for forming uniform ice-hockey-puck-shaped crystals.

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References