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Selective and rapid capture of Sr$^{2+}$ with LTA zeolites: Effect of crystal sizes and mesoporosity

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ABSTRACT

Zeolite LTA (Linde Type A) is a highly aluminous material (Si/Al = 1) that can be utilized for the removal of cationic radioactive element such as Sr$^{2+}$ (the homologues of $^{90}$Sr radionuclide) via the electrostatic interaction. Herein, a series of microporous LTA zeolites with controlled crystal sizes in a high uniformity was prepared for investigation of adsorption kinetics for Sr$^{2+}$ from seawater. Solely microporous LTA zeolites of various crystal sizes with 100 nm, 500 nm, and 2 µm were prepared by control of various synthetic parameters, and LTA zeolite having mesoporous structure with crystal size of 2 µm was also synthesized with an organosilane surfactant as the mesopore generating agent. The adsorption study for Sr$^{2+}$ from seawater using the LTA zeolites demonstrated that the different crystal size and mesoporosity gave a prominent influence on the adsorption performances that were compared numerically with the Lagergren 1st- and 2nd-order kinetic models. The resultant kinetic parameters revealed that the Sr$^{2+}$ adsorption kinetics followed 2nd-order model more preferentially than 1st-order one. Depending on the crystal sizes, the adsorption rate constant can be changed from 0.002 g mg$^{-1}$ min$^{-1}$ for the LTA with the largest size to 0.016 g mg$^{-1}$ min$^{-1}$ for the mesoporous LTA zeolite at 20 °C.

1. Introduction

Zeolites are crystalline ordered microporous materials consisting of aluminum and silicon covalently interconnected by oxygen atoms [1–5]. The trivalent aluminum species incorporated inside the SiO$_2$ framework generates one cation charge deficiency per one aluminum atom, by which the zeolites possess negatively charged surfaces that can be compensated by various types of cations such as H$^+$, alkali metal cations and transition metal cations [1–5]. Zeolites are widely used in various heterogeneous catalytic reactions (petrochemical cracking, isomerization and hydrocarbon synthesis), waste water treatment (sorption of toxic metals/radionuclides and pollutant chemicals), gas separation, sensing materials and even in medical fields [5–8]. Synthetic zeolites have clearly advanced the heterogeneous catalysis and separation processes because of their wide spectrum of framework structure and tunable porous networks. This constructs the family of zeolites consisting of more than 200 framework types [5–10]. Development of synthetic technologies enables the synthesis of various types of zeolites possessing different shapes, sizes, porosities and compositions [4,9]. Various synthesis methods such as hydrothermal, micro-reactors and microwave-mediated routes have received much attention, among which the hydrothermal synthetic route is considered as the most facile procedure for the synthesis of zeolites due to its adaptability in control of various synthetic parameters [4].

When zeolites are applied in adsorption and catalysis, not only the chemical composition and the pore architecture, but also the size and shape of the zeolite crystal give a significant influence on the adsorptive and catalytic performances [6–10]. Such adsorptive and catalytic applications are always involved with the diffusion kinetics of guest species into the zeolite framework, and thus the zeolite performances should be affected by the size and shape of crystal and pore of zeolites. Numerous research works on the control of zeolite properties including size, shape and mesoporosity have been reported. Zeolite crystal sizes can simply be controlled by modification of synthetic parameters such as pH, content of cationic species, silica and alumina precursors, and the synthesis conditions (i.e., aging time of synthesis gel, hydrothermal temperature and time, etc.) [11–13]. Secondary mesopores in addition to the intrinsic micropores can also be introduced to the zeolite framework, which constructs a hierarchically microporous and mesoporous zeolite architecture [14–21]. Various synthetic technologies have been reported for this purpose, which can be classified into post-demetallation method, soft-templating and hard-templating method, and dual-porogenic route [14–21].

Linde Type A (LTA) is one of the highly useful low silica-alumina...
The LTA zeolite is classified as small-pore zeolite with 3–5 Å of micropore aperture depending on the counter cation in the framework. Although the highly aluminous zeolite framework is not useful as the catalyst due to the deficiency of acidity, LTA zeolites are very useful for adsorption and separation processes due to the large density of cation capturing sites on the surface of zeolite framework. Due to its remarkable cation-exchange capacity of highly aluminous framework, LTA zeolites have efficiently been exploited in water softening (for the synthesis of laundry detergent) and in preparation of zeolite membranes for purification and separation processes (e.g., pervaporation; separation of mixtures of liquids) [24–28]. Moreover, LTA zeolites are also useful in the removal of toxic metal ions/radionuclides from aqueous media (water treatment) [25–26].

LTA zeolites can be synthesized into various sizes and morphologies with various Si/Al ratios beyond the traditional Si/Al ratio of 1 [27,29–30]. Control of pH, synthesis condition, and precursors of silica and alumina is effective for the synthesis of LTA zeolites with controlled size, shape and composition [13]. Aging time of the gel and condition of hydrothermal treatment can also affect the final property of LTA zeolite [13]. In particular, LTA zeolites can be synthesized to possess secondary mesopores with controlled mesopore diameters with the addition of organosilane surfactant as the mesopore generating agent [17]. Since the LTA zeolites are classified as a small-pore zeolite due to the 8-membered-ring pore aperture, the diffusivity of guest species into the LTA zeolite framework can be significantly affected by the size and porosity of LTA zeolite crystals. Although various synthetic methods for the control of size and mesoporosity of LTA zeolites have been developed, their effects on specific applications have not been systematically investigated.

Herein, the effect of LTA zeolite crystal size and the presence of mesoporosity on the selective removal of Sr\(^{2+}\) from seawater, Sr\(^{2+}\) is the homologues of \(^{90}\)Sr radionuclide whose kinetic diameter is ca. 1.18 Å, and thus its diffusivity into the framework of LTA zeolite should be significantly affected by the crystal size and the presence of mesoporous channels. For systematic investigation, a series of LTA zeolites with different crystal sizes in a high uniformity have been synthesized by controlling the synthetic parameters [13]. In order to investigate the role of mesoporous channel, LTA zeolite having secondary mesopores is also synthesized with the addition of organosilane surfactant in comparison with the counterpart with similar crystal size but without mesopores [17]. With the series of LTA zeolites prepared systematically in this work, the adsorption kinetics and thermodynamics have been studied during selective capture of Sr\(^{2+}\) from seawater condition. The adsorption results for various LTA zeolites were compared with various numeric parameters derived from the adsorption studies, which clarified the differences in adsorption capacity, rate and selectivity for the LTA zeolites with different sizes and mesoporosity.

2. Experimental

2.1. Chemicals

Sodium aluminate (NaAlO\(_2\), Sigma-Aldrich, 53% Al\(_2\)O\(_3\)) or aluminum isopropoxide (Alcohol, \(\geq 98\%\)) were used as the alumina precursor. Sodium metasilicate (Na\(_2\)O\(_3\)Si\(_9\)H\(_2\)O, Aldrich) or colloidal silica (Ludox HS-40, 40 wt% suspension in H\(_2\)O) were used as the silica precursor. Sodium hydroxide (NaOH, Daejung, > 97%) and tetramethylammonium hydroxide (TMAOH, Sigma-Aldrich, 25 wt% in H\(_2\)O) were used as the base sources. Dimethylmaleatedicyclo[13-(trimethoxyxlyl)]propylammonium chloride solution (DMOAP, Aldrich, 42 wt% in methanol) was used as a mesopore generating agent to synthesize mesoporous LTA crystals. The salts of sodium chloride (NaCl, Sigma-Aldrich, \(\geq 99.0\%\)), magnesium sulfate (MgSO\(_4\), Sigma-Aldrich, anhydrous, \(\geq 99.5\%\)), potassium chloride (KCl, Sigma-Aldrich, \(\geq 99.0\%\)), calcium chloride (CaCl\(_2\), Sigma-Aldrich, anhydrous, granular, \(\leq 7.0\) mm, \(\geq 93.0\%\)), and strontium chloride hexahydrate (SrCl\(_2\)·6H\(_2\)O, Junsei, 99.00%) were used for the preparation of seawater.

2.2. Synthesis of LTA zeolites with average crystal sizes of 111 nm and 491 nm

LTA zeolites with controlled crystal sizes were synthesized by following the literature published elsewhere [13]. The gel composition of 6.12 Si\(_2\)O\(_5\)/0.16 NaOH/1.0 Al\(_2\)O\(_3\)/345 H\(_2\)O/14.58 TMAOH was used for the synthesis of LTA zeolites with controlled crystal sizes of 100 nm. In a typical synthesis, 0.22 g of NaOH and 182.30 g of TMAOH were dissolved in 58.4 g of distilled water in polypropylene bottle. The solution was divided into two equal volumes in two different polypropylene bottles. Then, 14.09 g of aluminum isopropoxide was added to one bottle, and 31.7 g of colloidal silica was added to another. Both solutions were stirred separately until the solution becomes transparent. Silicate solution was then poured into the aluminate solution, and stirred until clearly mixed. The resulting solution continuously stirred for 3 days at room temperature and then transferred to the Teflon-lined stainless-steel autoclave. Hydrothermal crystallization was carried out at 100 °C for 24 h at the tumbling rate of 60 rpm. After crystallization, the sample was washed with distilled water by repeating dispersion-ultrasanocation-centrifugation (10,000 rpm, 10 min.), dried at 100 °C for 12 h and calcined in the presence of air at 550 °C for 3 h. The resultant nanocrystalline LTA zeolite is denoted as nLTA(111 nm) hereafter, in which the number in the parenthesis indicates the average crystal size of LTA zeolite determined by field emission scanning electron microscopy (SEM).

For the synthesis of LTA zeolite with average crystal size of 500 nm, the gel composition of 6.12 Si\(_2\)O\(_5\)/0.16 NaOH/1.0 Al\(_2\)O\(_3\)/345 H\(_2\)O/14.58 TMAOH was used. The rest of the synthesis conditions were kept similar to the nLTA(111 nm) except aging time. After mixing the two separate solutions of silicate and aluminate, the resultant mixture was directly transferred to the Teflon-lined stainless-steel autoclave and proceeded to hydrothermal synthesis. The resultant nanocrystalline LTA zeolite is denoted as nLTA(491 nm) hereafter.

2.3. Synthesis of LTA zeolite with average crystal size of 2 μm

The aluminosilicate hydrogel with a composition of 100 Si\(_2\)O\(_5\)/333 Na\(_2\)O/67 Al\(_2\)O\(_3\)/20000 H\(_2\)O was prepared by mixing the separate aluminate and silicate solutions. In this synthesis composition, organic base (i.e., TMAOH) was not used at all. In a typical synthesis, 4.28 g of NaOH was dissolved in 100 g of distilled water and 5.50 g sodium metasilicate was added to the aqueous NaOH solution (solution 1). In the resultant propylene bottle, 5.37 g of sodium aluminate was added to 50 g of distilled water and stirred until dissolved (solution 2). Solution 1 was mixed in solution 2 and the resultant mixture was vigorously shaken for 15 min. and transferred to the Teflon-lined stainless-steel autoclave. Hydrothermal synthesis was carried at 100 °C for 4 h under static condition. After crystallization, the sample was washed with distilled water by repeating dispersion-ultrasanocation-centrifugation (10,000 rpm, 10 min.). The obtained product was dried at 100 °C 12 h and calcined in the presence of air at 550 °C for 3 h. The resultant bulk LTA zeolite is denoted as bLTA(2 μm) hereafter.

2.4. Synthesis of mesoporous LTA zeolite with average crystal size of 2 μm

Mesoporous LTA zeolite was synthesized with the addition of organosilane surfactant as the mesopore generating agent by following the literature published elsewhere [17]. The aluminosilicate gel composition of 100 Si\(_2\)O\(_5\)/333 Na\(_2\)O/67 Al\(_2\)O\(_3\)/20000 H\(_2\)O/8 DMOAP was prepared by mixing separate aluminate and silicate solutions. In a typical synthesis, 4.28 g of NaOH was dissolved in 100 g of distilled water in a polypropylene bottle with the further addition of 5.50 g sodium
metasilicate and stirred until the clear solution obtained. Thereafter, 4.45 mL of DMOAP was added to the previous solution (silicate solution). In another polypropylene bottle, 5.37 g of sodium aluminate was added to 50 g of distilled water and stirred until completely dissolved. The rest of the synthesis conditions were kept similar to the \( \text{bLTA}(2 \, \mu\text{m}) \). The obtained product was dried at 100 °C 12 h and calcined in the presence of air at 550 °C for 3 h. The resultant mesoporous LTA zeolite is denoted as m\( \text{LTA}(2 \, \mu\text{m}) \) hereafter.

2.5. Characterisation

LTA zeolites were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM) analysis. XRD patterns were recorded on a 3-D high resolution X-ray diffractometer/EMPYREAN/PC equipped with Cu 1.8 kW radiation (Max. 60 kV, 55 mA) and Pixelcel 3D with prefix interface Xenon proportional detector at the rate 8'/min over the range of 2θ value 5–40°. The SEM imaging was done with a Hitachi Technologies S-4700 microscope with secondary electron image resolution. The TEM analysis was performed with a TECNAI F20 [Philips] microscope operated at 200 kV (Line resolution of 0.10 nm). Images were recorded with camera at high magnification and low-dose conditions. The Si/Al ratio of the LTA zeolite samples synthesized in this work was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific ICAP 6300 DuO).

2.6. Adsorption experiments

2.6.1. Preparation of seawater

In a 60 mL polypropylene bottle, 1.27 g (464.3 mmol) of sodium chloride, 4.45 g (37 mmol) of magnesium sulfate, 0.75 g (10 mmol) of potassium chloride and 1.1 g (10 mmol) of calcium chloride were added to 10 mL of distilled water. Subsequently, the stock solution of \( \text{Sr}^{2+} \) was prepared by adding 2 g (7.524 mmol) of strontium chloride hexahydrate to the former solution.

2.6.2. Batch adsorption experiments under seawater condition

Batch adsorption method was applied for adsorption studies of \( \text{Sr}^{2+} \) by synthesized LTA zeolites, i.e., n\( \text{LTA}(111 \, \text{nm}) \), n\( \text{LTA}(491 \, \text{nm}) \), b\( \text{LTA}(2 \, \mu\text{m}) \) and m\( \text{LTA}(2 \, \mu\text{m}) \). Prior to the adsorption experiments, all the LTA zeolites were ion-exchanged into Na\( ^+ \)-form. For ion exchange to Na\( ^+ \), LTA zeolites were mixed with 0.1 M NaNO\(_3\) aqueous solution, where the amount of Na\( ^+ \) in aqueous solution is set by 10 times larger than the amount of aluminum in LTA zeolite. The solution was stirred for 2 h at ambient conditions, then collected with centrifuge, and dried in an oven at 100 °C for overnight. The similar ion-exchange process was repeated for three times, and then the resultant zeolites were used for further experiments. In a typical adsorption experiment, 1 g of LTA zeolite in the Na\( ^+ \)-form was dispersed in 90 g of distilled water in a 200 mL polypropylene bottle and stirred for 10 h to make a proper suspension. 10 mL of concentrated seawater containing 7.524 mmol of strontium chloride was added to the LTA zeolite suspension, and the resulting suspension was stirred at 20 °C. All the adsorption experiments were carried out in the water bath whose temperature was controlled very steadily by a proportional-integral-differential (PID) temperature controller. Preliminary adsorption experiments showed that the adsorption under seawater condition reached the equilibrium after 2 h at 20 °C. After the adsorption experiments, the concentration of \( \text{Sr}^{2+} \) remained in the solution was analyzed using Atomic Absorption Spectrophotometer (AAS, Elmer AA-800 Atomic Absorption Spectrometer) to obtain the adsorption capacity and selectivity of zeolite samples.

2.6.3. Kinetic adsorption experiments

For kinetics study, an aqueous solution containing \( \text{Sr}^{2+} \) with concentration of 365 mg L\(^{-1}\) in a distilled water was prepared. In 1.0 L of this solution, 1.0 g of LTA zeolite samples was added, and a fixed amount of aliquots from each sample were withdrawn and filtered by using syringe filter at definite time intervals. Subsequently, the concentration of \( \text{Sr}^{2+} \) ions in the aliquot suspension was determined by AAS. A series of adsorption experiments were conducted at different temperatures (20 °C and 40 °C), of which the kinetics were interpreted with the Lagergren kinetic model [31–34].

3. Results and discussion

3.1. Characterisation of LTA zeolites

Fig. 1 shows the wide-angle XRD patterns of four LTA zeolite samples synthesized in this work (i.e., n\( \text{LTA}(111 \, \text{nm}) \), n\( \text{LTA}(491 \, \text{nm}) \), b\( \text{LTA}(2 \, \mu\text{m}) \) and m\( \text{LTA}(2 \, \mu\text{m}) \)). The numbers in parentheses corresponded to Miller indices.

Fig. 1. Powder XRD patterns of four LTA zeolites synthesized in this work (i.e., n\( \text{LTA}(111 \, \text{nm}) \), n\( \text{LTA}(491 \, \text{nm}) \), b\( \text{LTA}(2 \, \mu\text{m}) \) and m\( \text{LTA}(2 \, \mu\text{m}) \)). The numbers in parentheses corresponded to Miller indices.

The SEM images in Fig. 2 show the clear differences of zeolite crystal sizes and uniformity for four LTA zeolite samples. Fig. 2(A–D) show the low-magnification SEM images for n\( \text{LTA}(111 \, \text{nm}) \), n\( \text{LTA}(491 \, \text{nm}) \), b\( \text{LTA}(2 \, \mu\text{m}) \) and m\( \text{LTA}(2 \, \mu\text{m}) \), respectively, which show the distribution of zeolite crystal sizes with respective histograms (insets in Figs. (A–D)). The low-magnification SEM images demonstrated that all the synthesis done in this work gave very uniform LTA zeolite crystals with controlled sizes. The crystal size distributions of four LTA zeolites were obtained by counting 150 individual zeolite particles, which gave the average values of 111 nm, 491 nm, 2 \( \mu\text{m} \) and 2 \( \mu\text{m} \) for n\( \text{LTA}(111 \, \text{nm}) \), n\( \text{LTA}(491 \, \text{nm}) \), b\( \text{LTA}(2 \, \mu\text{m}) \) and m\( \text{LTA}(2 \, \mu\text{m}) \), respectively. No amorphous phases were observed for all the samples over the low-resolution and high-resolution SEM images. The high-magnification SEM images in Fig. 2(E–H) enable the more accurate
observation of surface and morphology of individual LTA zeolite crystals, which demonstrated that the typical single-crystalline cubic shape of LTA zeolite crystal is highly maintained in zeolite samples having bigger crystal sizes (i.e., bLTA(2 µm) and mLTA(2 µm)). However, the sharp edge of cubic crystal became broadened gradually as the crystal size decreased to 491 nm and 111 nm. In addition, as compared with the LTA zeolites with very smooth surface for nLTA(111 nm), nLTA(491 nm) and bLTA(2 µm) samples, the surface of the mLTA(2 µm) is not smooth but very tiny particles are aggregated with interparticle spaces that corresponded to the intercrystalline mesopores.

The internal structures of four LTA zeolites are shown in TEM images (Fig. 2(I–L)). From the TEM images of nLTA(111 nm), nLTA(491 nm) and bLTA(2 µm), well-ordered crystalline lattice fringes are observable with sharp edges corresponding to the cross-section of (1 0 0) lattice plane. Between the lattice fringes, very narrow channel corresponded to the microporous channel of LTA zeolite framework. In the case of mLTA(2 µm), the internal structure is totally different as compared to the former three zeolite samples. There are white void spaces constructed by aggregation of small nanoparticles (Fig. 2(L)), which are the intercrystalline mesopores. Although crystalline lattice fringes are not clearly observable, the small nanoparticles corresponded to the crystalline zeolite framework as proved by the presence of electron diffraction pattern (Fig. 2(L) inset).

3.2. Selective removal of Sr\textsuperscript{2+} from seawater condition

Selective adsorption experiments of Sr\textsuperscript{2+} ions using the LTA zeolites synthesized above were performed in aqueous solutions containing general seawater components such as Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, K\textsuperscript{+} and Na\textsuperscript{+}. This experiment could give the adsorption affinity and selectivity of zeolite samples to Sr\textsuperscript{2+} in competition with other cations under seawater condition. The graphs in Fig. 3 show the adsorption results of four zeolite samples in comparison with blank solution without the zeolite adsorbents. The residual concentrations (ppm) of Sr\textsuperscript{2+} in the seawater after the adsorption experiments were graphitized in Fig. 3(A). The residual concentration of Sr\textsuperscript{2+} in the blank solution without any zeolite adsorbents was maintained, which indicated that the Sr\textsuperscript{2+} is not removed or disappeared by vaporization or adsorption by the solution bottles. The residual concentration of Sr\textsuperscript{2+} in the solution could be converted to the adsorption amounts of Sr\textsuperscript{2+} by the zeolite samples. Fig. 3(B) shows the adsorbed amount of four zeolite samples in percent concentration, which indicated a significant difference in adsorption capacity for four zeolite samples. The nLTA(111 nm) and nLTA(491 nm) showed very lower adsorption capacity, where two zeolites could capture only about 23% and 7% of Sr\textsuperscript{2+}, respectively. However, bLTA(2 µm) and mLTA(2 µm) zeolites showed much better adsorption performance, where more than 80% of Sr\textsuperscript{2+} in the seawater could be removed very selectively.

Such a difference in the adsorption capacities and thus the selectivity to Sr\textsuperscript{2+} in the competitive seawater environment might be
attributed to the difference in crystallinity and hence the difference in the adsorption sites (i.e., aluminum in the zeolite framework). Of four zeolite samples, the bLTA(2 µm) zeolite showed the highest crystallinity in terms of XRD analysis and SEM investigation. On the contrary, the nanocrystalline nLTA(111 nm) and nLTA(491 nm) zeolite samples were relatively less crystalline as observed in SEM images (Fig. 2(E–F)). The cubic morphologies of typical LTA zeolite crystal were not clearly constructed in both nanocrystalline LTA zeolite samples. Therefore, it is highly probable that the aluminum sites were not perfectly incorporated inside the zeolite framework. Indeed, though the typical Si/Al ratio of fully crystalline LTA zeolite framework is 1, the actual Si/Al ratios of nLTA(111 nm) and nLTA(491 nm) zeolite samples were analyzed to 1.7 and 1.6, respectively. In the case of bLTA(2 µm) and mLTA(2 µm) zeolites, their Si/Al ratios were 1.2 and 1.3, respectively. Accordingly, the divalent Sr$^{2+}$ cations could be more selectively captured by LTA zeolites in the competitive adsorption environment of seawater containing various monovalent and divalent cations.

3.3. Adsorption kinetic modeling

The adsorption kinetics of four LTA zeolite samples were investigated in distilled water containing Sr$^{2+}$ ions by following the adsorption quantity as the function of adsorption time during the adsorption process (min) with the equilibrium adsorption quantity at 20 °C and 40 °C. Fig. 4(A) shows the adsorption isotherms for four zeolite samples as a function of adsorption quantity versus adsorption time at 20 °C. The results show that all the zeolite samples exhibited very rapid capture of Sr$^{2+}$ ions from distilled water, of which the adsorption quantity reached the equilibrium within 10 min. Of four adsorption isotherms, the mLTA(2 µm) exhibited the steepest increase of adsorption capacity before 1 min, whereas the others exhibited relatively more moderate increase of adsorption capacity along the adsorption period of 5 min. The adsorption isotherms for four zeolite samples were further analyzed with the Lagergren kinetic model (Fig. 3(B-C)). The adsorption kinetics in Fig. 4(A) can be applied to either pseudo 1st-order or 2nd-order kinetic models [31–34].

The 1st-order equation can be expressed as follows,

$$\log (q_t - q) = \log q_e - (k_1/2.303)t$$

where $q_t$ and $q$ are the respective amounts of Sr$^{2+}$ adsorbed on the zeolite (mg g$^{-1}$) at equilibrium and at time $t$, and $k_1$ is the pseudo 1st-order rate constant (min$^{-1}$). Applying this equation to the adsorption isotherm in Fig. 4(A), the plots of log ($q_t - q$) versus $t$ for four LTA zeolites could be graphitized in Fig. 4(B). From the linear fittings, the slopes and intercepts of the plots could be derived to determine the values of 1st-order rate constant ($k_1$) and the simulated adsorption capacities at equilibrium ($q_e$,sim), respectively, which were summarized in Table 1.

The 2nd-order equation can be expressed as follows,

$$\frac{t}{q_e} = \frac{1}{(k_2q_e^2)} + \frac{t}{q_e}$$

where $k_2$ is the rate constant of pseudo 2nd-order equation (g mg$^{-1}$ min$^{-1}$). Fig. 4(C) shows the plots of $t/q$ versus $t$ for four zeolites, from which the slopes and intercepts of the plots could be derived to determine the values of 2nd-order rate constant ($k_2$) and the simulated adsorption capacities at equilibrium ($q_{e, sim}$), respectively, which were summarized in Table 1. The parameter “$h$” in Table 1 is the initial sorption rate could be derived from the product of 2nd-order rate constant ($k_2$) and the simulated adsorption capacities at equilibrium ($q_{e, sim}$), i.e., $h = k_2 q_e^2$.

All the adsorption parameters at 20 °C derived from the linear fitting of the plots using 1st- and 2nd-order equations (Fig. 4(B–C)) are summarized in Table 1, in comparison with the experimental adsorption capacity ($q_{e, exp}$) at equilibrium. The applicability of linear plots can be determined by the correlation coefficients ($R^2$), where the 1st-order linear fittings gave 0.955–0.971 of $R^2$. In contrast, 2nd-order linear fittings gave the coefficients more than 0.995 that is very close to 1, which suggested that the 2nd-order kinetic model is more applicable and appropriate to fit the experimental data. The applicability can also be determined by the comparison of the simulated adsorption capacity ($q_{e, sim}$) with experimental one ($q_{e, exp}$) at equilibrium. As summarized in Table 1, the simulated adsorption capacities ($q_{e, sim}$) for four zeolite samples derived from the 1st-order kinetics are much smaller than the experimental adsorption capacities ($q_{e, exp}$). However, the experimental adsorption capacities can be matched much better with the simulated values derived from the 2nd-order kinetics. This indicates that the adsorption of Sr$^{2+}$ ions by the LTA zeolites can be explained with 2nd-order kinetic model more applicably than with 1st-order one.

From the parameters derived from the 2nd-order equation, the effects of crystal size and mesoporosity on the adsorption kinetics can be numerically compared. Among three LTA zeolites having solely microporous structure without secondary mesopores (i.e., nLTA(111 nm), nLTA(491 nm) and bLTA(2 µm)), nLTA(111 nm) exhibited the fastest adsorption rate with rate constant ($k_2$) of 0.014 g mg$^{-1}$ min$^{-1}$. The rate constant decreased significantly to 0.007 and 0.002 for nLTA(491 nm) and bLTA(2 µm), which was proportional to the increase of average crystal size. This clearly indicated that the adsorption rate of Sr$^{2+}$ ions increased as the average crystal size of LTA zeolite decreased. In addition, with the comparison of bLTA(2 µm) and mLTA(2 µm), the effect of mesoporos on the adsorption kinetics could be investigated. These two LTA zeolites were synthesized into the similar average crystal size of 2 µm, but one is solely microporous and the other is hierarchically microporous/ mesoporous. The mLTA(2 µm) sample showed the fastest adsorption rate with rate constant of 0.016 g mg$^{-1}$ min$^{-1}$. In contrast, bLTA(2 µm) showed the slowest adsorption rate with rate constant of 0.002 g mg$^{-1}$ min$^{-1}$. This result indicates that the presence of mesopores in the zeolite crystal could increase the diffusivity of guest species.

Fig. 4. (A) Adsorption isotherms of nLTA(111 nm) (black), nLTA(491 nm) (red), bLTA(2 µm) (blue) and mLTA(2 µm) (pink) during adsorption of Sr$^{2+}$ at 20 °C according to the adsorption time (min), (B) plots of log ($q_t - q$) versus $t$ based on the 1st-order kinetic equation, and (C) plots of $t/q$ versus $t$ based on the 2nd-order kinetic equation.
that could increase the adsorption rate of Sr$^{2+}$ ions.

In the case of adsorption capacities, bLTA(2 µm) zeolite sample showed the largest adsorption capacity with 204.3 mg g$^{-1}$ from the adsorption experiment. In contrast, other three LTA zeolite samples showed the less adsorption capacity with around 150 mg g$^{-1}$. Such a difference in the equilibrium adsorption capacities might be attributed to the difference in crystallinity. Of four zeolite samples, the bLTA(2 µm) zeolite showed the highest crystallinity in terms of XRD analysis and SEM investigation. On the contrary, the nanocrystalline nLTA(111 nm) and nLTA(491 nm) zeolite samples were relatively less crystalline as observed in SEM images (Fig. 2(E–F)). The cubic morphologies of typical LTA zeolite crystal were not clearly constructed in both nanocrystalline LTA zeolite samples. In the case of mLTA(2 µm), though this zeolite maintained the single crystalline cubic morphology (Fig. 2(H)) similar to the bLTA(2 µm), the individual zeolite particles constructing the cubic aggregate were less crystalline as observed in TEM image (Fig. 2(L)). Such a deficiency of full crystallinity in nLTA(111 nm), nLTA(491 nm) and mLTA(2 µm) zeolite samples might decrease the adsorption affinity of aluminum sites to Sr$^{2+}$ ions, as compared to the bLTA(2 µm) zeolite having full crystallinity with cubic shape.

The adsorption experiments were also carried out at higher adsorption temperature of 40 °C, from which the resultant adsorption isotherms were drawn in Fig. 5(A). The adsorption profiles according to the adsorption time followed similar trends of adsorption results at 20 °C, in which the adsorption reached the equilibrium very rapidly. The adsorption isotherms could also be analyzed with the aforementioned Lagergren kinetic models, where the 1st- and 2nd-order linear fitting results were plotted in Fig. 5(B) and (C), respectively, and the derived parameters were summarized in Table 2. As proposed in the adsorption analysis at 20 °C, the adsorption of Sr$^{2+}$ to the LTA zeolites also followed the 2nd-order model more applicable than 1st-order one. The correlation coefficients ($R^2$) derived from the 2nd-order model were close to 1, indicating that the 2nd-order model is much more appropriate than the 1st-order one. In addition, the simulated adsorption capacities derived from the 2nd-order model were close to the actual adsorption capacities from the adsorption experiments, indicating that the adsorption of Sr$^{2+}$ to the LTA zeolites at higher adsorption temperature also followed 2nd-order kinetics more preferably than 1st-order one.

The adsorption rate constants calculated from the 2nd-order kinetic model at 40 °C were much larger than those calculated at 20 °C. In particular, the initial adsorption rates ($h$) were also much larger at 40 °C than 20 °C. Such increases in rate constants and the initial adsorption rates according to the increase of adsorption temperature indicated that the adsorption of Sr$^{2+}$ to the zeolite surface is governed by an endothermic process.

4. Conclusions

We have synthesized a series of LTA zeolites with controlled crystal sizes and mesoporosity. Two nanocrystalline LTA zeolites with hundreds nanometers in average size (i.e., nLTA(111 nm) and nLTA(491 nm)) were prepared by control of synthetic parameters and hydrothermal conditions. Two types of micron-size LTA zeolites with or without secondary mesoporous structure were synthesized, where the one is bLTA(2 µm) with average crystal size of 2 µm having solely microporous structure in a highly crystalline cubic morphology and the other is mLTA(2 µm) with similar crystal size but having hierarchically microporous/mesoporous structure. The four LTA zeolites with different crystal sizes and mesoporosity were applied to the adsorption experiments to capture Sr$^{2+}$ from seawater to investigate the adsorption capacity and selectivity. The results show that the crystal size, mesoporosity and crystallinity played an important role on adsorption capacity and selectivity, where the bLTA(2 µm) and mLTA(2 µm) zeolites exhibited the highest capacity with greater than 80% adsorption selectivity. The kinetic studies for adsorption of Sr$^{2+}$ to the zeolites from distilled water were also carried out to compare the adsorption performances of four LTA zeolites with adsorption parameters derived from the Lagergren kinetic models. The results indicated that the adsorption of Sr$^{2+}$ could be explained with the 2nd-order kinetic model more applicable than 1st-order one. The small size of zeolite crystal or

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**Table 1**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>1st-order kinetic parameters</th>
<th>2nd-order kinetic parameters</th>
<th>qe,exp (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_{e,calc}$ (mg g$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>nLTA(111 nm)</td>
<td>0.354</td>
<td>131.3</td>
<td>0.955</td>
</tr>
<tr>
<td>nLTA(491 nm)</td>
<td>0.211</td>
<td>83.2</td>
<td>0.966</td>
</tr>
<tr>
<td>bLTA(2 µm)</td>
<td>0.093</td>
<td>132.2</td>
<td>0.971</td>
</tr>
<tr>
<td>mLTA(2 µm)</td>
<td>0.132</td>
<td>38.3</td>
<td>0.970</td>
</tr>
</tbody>
</table>

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Fig. 5. (A) Adsorption isotherms of nLTA(111 nm) (black), nLTA(491 nm) (red), bLTA(2 µm) (blue) and mLTA(2 µm) (pink) during adsorption of Sr$^{2+}$ at 40 °C according to the adsorption time (min), (B) plots of log ($q_e - q$) versus $t$ based on the 1st-order kinetic equation, and (C) plots of $t/q$ versus $t$ based on the 2nd-order kinetic equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the presence of mesopores were advantageous for rapid adsorption of Sr²⁺ with high rate constants. In addition, the adsorption parameters derived at different adsorption temperatures proposed that the adsorption is governed by an endothermic process. The results described in this work could shed light on the fundamental understanding of adsorption phenomenon using the well-designed adsorbent system constructed by LTA zeolites with controlled sizes and mesoporosity, which could be further applied to the design of zeolite-based adsorbents for selective and rapid removal of cation-type radioactive elements.

Author Contributions

K. Na initiated, conceptualized and administrated the research with funding acquisition. S. Kwon and Y. Choi carried out all the experiments including characterizations and data curation, B. K. Singh participated in the preparation of manuscript with K. Na.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References