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Eco-friendly synthesis of zeolite A from synthesis cakes prepared by removing the liquid phase of aged synthesis mixtures

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Zeolite can be synthesized through hydrothermal reaction of a synthesis cake prepared by removing the liquid phase from a synthesis mixture. The volume and weight of the synthesis cake prepared using a filter press were about one-eighth and one-fourth those of the mixture, respectively. This implies that the reactor volume and energy input required for the hydrothermal reaction can be reduced by the same respective factors, allowing the eco-friendly synthesis of zeolite.

Zeolites have widely been used in industry and in households as catalysts, adsorbents, and detergent builders.[1-5] The micropores in their particular crystalline frameworks provide uniform pore entrances and large surface areas for reactants and adsorbates. The rapid replacement of the calcium and magnesium ions in water with sodium ions contained in zeolites converts hard water to soft water, thus enhancing the washing power of detergents.[6] The applications of crystalline nanoporous zeolites have continuously been expanded thanks to the high potential for adjustment of the physico-chemical properties such as adsorption, acid-base, and cation exchange.

There is huge global consumption of synthetic zeolites, and it has been increasing continuously from 2.87 million tons in 2011.[7] Among the types of zeolite with various frameworks, zeolite A with the LTA framework has largely been used as an effective detergent builder which does not cause water pollution through processes such as eutrophication, as do phosphate detergent builders. In addition, zeolite A is a well-known adsorbent, with applications such as 3A, 4A and 5A molecular sieves used to remove water from various solvents and industrial raw materials. This strong versatility has expanded the applications of zeolite A to occupy 73% of the total production of synthetic zeolites, ranking it as an important inorganic chemical.[8]

Zeolite A has typically been synthesized through the hydrothermal reaction of synthesis mixtures prepared by mixing the sources of silica and alumina, alkaline species, and water, as for other zeolites. The synthesis mixtures charged in a sealed autoclave are heated under autogenous pressures at 60-100 °C. The composition of the synthesis mixtures, in terms of silica, alumina, alkali, and water content, and the reaction conditions, including temperature, time, and heating method, determine the rate of crystallization, as well as the morphology and size distribution of the zeolite A particles obtained. The hydrothermal reaction is suited for large-scale operation, and has thus become the most common method for zeolite A manufacture. However, this conventional method has several disadvantages. The low contents of silica and alumina in a large amount of water necessitate the use of a large reactor, and accordingly, a large amount of energy, to carry out the reaction. Furthermore, the use of water to wash alkaline species off the synthesized zeolite A particles produces large emissions of alkaline wastewater.

In order to reduce the water content of the synthesis mixtures, the use of extremely dense synthesis mixtures has been suggested for the synthesis of zeolite A, but excessively small water quantities hinder the preparation of homogeneous mixtures with mechanical stirrers due to dust generation.[9] The synthesis of zeolites such as MFI, MTN and MTW, even from dried reactants, was reported considerably earlier.[10,11] The water formed between reactants at elevated temperatures mediated the crystallization of zeolites. Recently, a method for the solvent-free synthesis of zeolites by mixing, grinding, and heating of the solid raw materials was also reported as an effective way for ZSM-5 zeolite synthesis.[12] The direct use of solid raw materials enhances synthesis productivity and reduces the energy consumption for the thermal reaction. However, the previous papers did not address the application of such eco-friendly synthesis methods to zeolite A. Furthermore, the large heterogeneous aggregated zeolite particles synthesized from dried reactants are not suitable for the manufacture of detergent builders, because the size and shape of zeolite A are essential for application in terms of the exchange speed of cations, removal efficiency from clothes, and handling convenience. Particles sized 1-2 microns with round edges exhibit the best performance as detergent builders. Therefore, a new eco-friendly route for the synthesis of zeolite A with reduced energy requirements and improved productivity is strongly required.

The crystallization of zeolite A is generally considered to follow successive steps of nucleation and crystal growth.[13] Although the structure and size of nuclei are not definitely verified, the formation of nuclei is essential for zeolite crystallization, regardless of whether they are formed as a consequence of the supersaturation of source materials or the addition of seeds.[14] Simple ageing of synthesis mixtures of zeolite A, even at ambient temperatures, facilitates nuclei formation.[15] According to the solid-transformation mechanism, though not generally applicable to all types of zeolite, nuclei dispersed in a crystallizing gel consume the reactants to grow into zeolite particles. From these results, the liquid phase of synthesis mixtures makes a weaker contribution than the solid phase in the crystallization of zeolite A, while the hydrothermal reaction of synthesis cake prepared by removing the liquid phase from the synthesis mixture can result in the effective production of zeolite A with higher productivity and less energy.

Here, we developed a eco-friendly route for synthesizing zeolite A from synthesis cakes prepared by removing the liquid phase from the aged synthesis mixture through simple and forced filtering. A comparison of this new synthesis method with the conventional method is provided in Scheme 1. The key point of the new method is the change of material to be heated for hydrothermal reaction: only the solid phase collected from the synthesis mixture is heated, rather than the mixture itself. Since the volume and weight of the reactants are respectively reduced to about one-eighth and one-fourth after filter pressing, the reactor volume and energy input required for the hydrothermal reaction can be reduced by the same respective factors. Nonetheless, the amount of water remaining in the synthesis mixture is sufficient to achieve homogeneous mixing of the reactants, while the ageing process facilitates nuclei formation. The hydrothermal reaction of the synthetic cake enables control of the morphology and size distribution of the zeolite A produced.

We prepared a synthesis mixture with a composition of 1.0 Al_2O_3 : 1.9 SiO_2 : 3.2 Na_2O : 125 H_2O.[16] Photos of the initial and aged synthesis mixtures are shown in Fig. 1, along with the separated liquid phase and the synthesis cake after filtration. The as-prepared synthesis mixture was an opaque suspension, but a clear boundary was formed between the liquid and solid phases after ageing for 24 h at 15 ^oC. Only simple filtering was required to separate the two phases into a 53 wt% liquid filtrate and a 47 wt% synthesis cake. The synthesis mixture and cake were denoted as SM-SF and SC-SF, respectively, with SF standing for simple filtering. The volume of SM-SF was about twice that of SC-SF. The compositions of the synthesis cake and the filtrate were 1.0 Al_2O_3 : 2.1 SiO_2 : 2.2 Na_2O : 58.4 H_2O and 1.0 Al_2O_3 : 0.3 SiO_2 : 10.2 Na_2O : 602 H_2O, respectively. The major portions of silica (98%) and alumina (88%) supplied for the preparation of the synthesis mixture were retained in the synthesis cake, while 61% sodium hydroxide and 41% water were retained.

The crystallization of zeolite A can be monitored by the gradual increase of its characteristic diffraction peaks during hydrothermal reaction. Fig. 2 shows the X-ray diffraction (XRD) patterns of the solid phase collected after hydrothermal reaction of SM-SF and SC-SF at 70 ^oC for different periods of time. The small XRD peaks attributed to zeolite A at $2\theta = 7.2°$, 10.2°, 24.0°, 27.1°, and 29.9° on the solid phases from SM-SF obtained after 3 h of reaction and those from SC-SF obtained after 2.5 h of reaction confirmed the formation of zeolite A from both the synthesis mixture and the cake.[17] The XRD peaks gradually increased with increase of the reaction time until 5 h, indicating that it took 5 h for both the mixture and the cake to complete crystal growth at 70 ^oC.

Since the Si/Al mole ratio of zeolite A is one, all silicon and aluminum atoms in its frameworks have equal chemical environments, coordinated with the other four atoms through oxygen atoms in the form of Si-(O-Al)$_4$- or Al-(O-Si)$_4$-. Fig. S1 shows the magic angle spinning (MAS) NMR spectra of the zeolite A crystallized from SM-SF and SC-SF at 70 ^{o}C for 5 h. The presence of a single ^{29}Si MAS NMR peak at -90.3 ppm clearly indicated the equal chemical environments with tetrahedral coordination.[18] All silicon and aluminum atoms of the zeolite A synthesized from the synthesis cake composed a perfect tetrahedral framework.

In order to verify the presence of micropores in the LTA zeolite synthesized from the synthesis cake (SC-SF), its adsorption isotherm of nitrogen was compared with those of the zeolite from SM-SF and a commercial 4A molecular sieve (Linde, Linde 4A) as shown in Fig. S2. The fact that all the three Na-LTA zeolites showed very small amounts of adsorbed nitrogen indicates that the pore entrances of LTA zeolites containing sodium ions are too small to allow the transfer of nitrogen through. On the contrary, the adsorption isotherms on the calcium ion-exchanged LTA zeolites showed large amounts of adsorbed nitrogen for all the three types of zeolite alike, as indicated in the literature.[19] The surface areas of micropores in these zeolites were found by a BET analysis to be 470 m^2/g for Ca-SC-SF, 490 m^2/g for Ca-SM-SF, and 500 m^2/g for Ca-Linde-4A, and the pore volume found by a *t*-plot method to be 0.20 cm^3/g for all the types. Fig. S3 compares the adsorption isotherms of carbon dioxide on the three Na-LTA zeolites. Since carbon dioxide has a molecular size small enough to pass through the micropores of LTA zeolite, considerable amounts were adsorbed on each type of zeolites on similar levels. This again confirms that the LTA zeolite synthesized from the synthesis cake has the same micropore characteristics as the other two types of LTA zeolite.

The amount of zeolite A produced from SM-SF and SC-SF, as hydrated states, was 8.6 g per 100 g synthesis mixture and 18.5 g per 100 g synthesis cake, respectively. The high water content of the synthesis mixture reduced the productivity of zeolite A. However, the yields of zeolite A, defined by the percentages of the mass of silica in the zeolite A produced to the amount of silica in the synthesis mixture and cakes, were 66% and 68%, respectively. This yield similarity indicates that the crystallization was not significantly influenced by the amount of water present in the synthesis mixture and cake.

The crystallization of zeolite A from synthesis mixtures of crystallizing gel and liquid phase is well-known.[14] To the best of our knowledge, however, the crystallization from a synthesis cake which retained only a small amount of the liquid phase has not yet been reported. The similar crystallization behavior of SM-SF and SC-SF in terms of the rate and purity of zeolite A particles indicates that the crystallization mainly occurred in the solid phase, with little role played by the liquid phase. Since the weight and volume of SC-SF were smaller than those of SM-SF, the efficiency of the hydrothermal reaction in terms of reactor volume and energy requirement should be enhanced with SC-SF compared to SM-SF.

The crystallization rate of zeolites varies widely according to the reaction temperature, since temperature influences both the activity of the source materials and the rate constant of zeolite growth.[20] The crystallization curves of zeolite A from SM-SF and SC-SF at various temperatures are presented in Fig. 3, wherein the crystallinity was defined as the zeolite fraction of the solid phase collected after hydrothermal reaction. The crystallization of zeolite A from SM-SF was completed within 1.5 h at 90 ^{o}C, but was restricted to only 20% even after 16 h at 50 ^{o}C. The increase in temperature effectively accelerated the crystallization, but only small effect of temperature was observed above 80 ^{o}C. The overall crystallization curves of zeolite A from SC-SF were very similar to those from SM-SF, which further indicates that the crystallization from the synthesis cake proceeded similarly to that from the synthesis mixture regardless of temperature.

Fig. 4 compares the scanning electron microscopy (SEM) images of zeolite A obtained from SM-SF and SC-SF at 60 ^{o}C, 70 ^{o}C, 80 ^{o}C, and 90 ^{o}C. Most of the zeolite A particles were cubic with round edges, regardless of the starting material and synthesis temperature. The average particle size slightly increased with increase of the reaction temperature, indicating that further nucleation was somewhat suppressed while the nuclei formed during ageing started to grow faster at higher temperatures. The suppression at elevated temperatures was attributed to the difficulty in attaining supersaturation of the soluble species necessary for nucleation, as well as the shorter reaction times obtained.

If nuclei are assumed to be generated during an induction period (t_{ind}) covering from the ageing time to the early stage of crystallization for growth to detectable sizes, the growth rate constant (k_{grow}) for zeolite particles can be determined based on the observed crystallization curves. Since $Z^{1/3}$ corresponds to the size of the zeolite particles, a plot of $Z^{1/3}$ versus crystallization time will give a line with a slope that is proportional to k_{grow}. Such plots for the crystallization curves given in Fig. 2 are illustrated in Fig. S4, where the observed linear relationships validate our assumption. In addition, the temperature dependences of the crystal growth from the synthesis mixtures and cakes, i.e., the activation energy, could be determined from the Arrhenius plots of ln k_{grow} versus the reciprocal of temperature (Fig. S5). The activation energies determined from the approximately linear relationships (while the similar crystallization curves of zeolite A obtained at 80 ^{o}C and 90 ^{o}C resulted in slight deviations at the high temperature zone) were 79 and 66 kJ mol^{-1} for the growth from SM-SF and SC-SF, respectively. These values were obtained by excluding the k_{grow} at 90 ^oC, because this temperature was too high to induce further increases in k_{grow}. The similar activation energies for crystallization during synthesis from the mixture and cake reveal that crystal growth predominantly occurred in the crystallizing gel, i.e., the solid phase. The smaller activation energy for SC-SF was attributed to the proximity between the source materials in the cake, lowering the mass transfer barrier. The activation energy for the synthesis of zeolite A reported in the literature varies in the range of 44-79.5 kJ mol^{-1} according to the composition of the synthesis mixture and the aging treatment employed.[21-24] The results obtained herein were in the upper part of the literature values, likely because the activation energies determined herein accounted for only the growth stage of crystallization. The values of various parameters obtained from the aforementioned analysis of crystallization curves are summarized in Table 1.

To investigate the effects of composition on the crystallization of zeolite A, a different synthesis mixture composed of 1.0 Al_2O_3 : 2.0 SiO_2 : 2.5 Na_2O : 64 H_2O was also prepared. Compared with the previous synthesis mixture, SM-SF, the concentrations of alumina and silica were increased by 2-fold, while that of sodium hydroxide rose by 1.6-fold. This concentrated synthesis mixture and the cake obtained by filtering were denoted as SM-HC and SC-HC, respectively, with HC standing for high concentration. The XRD patterns obtained after the crystallization of SM-HC and SC-HC at 70 ^oC are shown in Fig. 5. Comparison with the XRD patterns obtained from SM-SF and SC-SF given in Fig. 2 did not reveal any significant differences, except that the first XRD peaks of zeolite A from SM-HC appeared 0.5 h later than those from SM-SF, while those from SC-HC appeared 0.5 h earlier than those from SC-SF. In all cases the crystallization was completed after the hydrothermal reaction for 5 h. However, the SEM photos of the zeolite A particles obtained from SM-HC and SC-HC, shown in Fig. S6, displayed considerable differences from those synthesized from SM-SF and SC-SF, shown in Fig. 4. In the case of the concentrated source materials, numerous particles smaller than 0.2 µm co-existed with large particles sized 1.0-1.5 µm, indicating that further nucleation proceeded along with the crystal growth during the hydrothermal reaction. This tendency was much more conspicuous in the crystallization of SC-HC than SM-HC. The enhanced nucleation can be explained by the increase in the solubility of the source materials due to high alkalinity, as well as the greater number of sodium cations acting as a structure-directing agent.

The water content of the synthesis cake also plays an important role in determining the type of zeolite produced. To investigate the effect in detail, five more synthesis cakes with lowered water contents of 64%, 54%, 41%, 33%, and 5% were prepared from SC-SF with 74% water using a vacuum freeze dryer for different amounts of times. Each cake was denoted by appending the water content, e.g., SC-SF64 for 64% water. Fig. 6 shows the XRD patterns of the zeolite samples obtained from these synthesis cakes at 70 ^oC for 9 h. SC-SF64 was found to produce perfect zeolite A, but the crystallinity of the zeolite A obtained from SC-SF54 was only about 60%, indicating that the lowered water content hindered the crystallization. In contrast, sodalite was predominantly produced from SC-SF41, SC-SF33, and SC-SF5. The higher alkalinity of the synthesis cakes due to the lowered water content favored the formation of sodalite, which has a denser framework than zeolite A.[25]

The results from the small lab-scale experiments described so far suggest that the crystallization from synthesis cakes rather than synthesis mixtures is an eco-friendly method for manufacturing zeolite A, requiring a smaller reactor and less energy input. To investigate the feasibility of the proposed method for large-scale production, 11 kg of synthesis mixture with the same composition as SM-SF was prepared, from which 2.6 kg of synthesis cake was obtained using a filter press under the forced pressure of 0.5-0.6 MPa. The cake obtained by this forced filtering was named SC-FF1, and its composition was determined to be 1.0 Al_2O_3 : 2.2 SiO_2 : 1.5 Na_2O : 22.9 H_2O. The liquid filtrate (SC-FFL1) was 8.4 kg, and had the composition of 1.0 Al_2O_3 : 0.4 SiO_2 : 13.1 Na_2O : 722 H_2O. The filtering lowered the water content from 74% in SC-SF to 56% in SC-FF1, thus increasing the alkalinity of SC-FF1. SC-FF1 only retained 16% of the initial water from SM-SF. In order to examine the possibility of controlling the size and shape of the zeolite A obtained by changing the alkalinity of the synthesis mixtures, another synthesis cake was then prepared from a synthesis mixture with 10% lower sodium hydroxide content (1.0 Al_2O_3 : 1.9 SiO_2 : 3.1 Na_2O : 128 H_2O), which was named SC-FF2. For SC-FF2, the ratios of the volume and weight reduction after the filter pressing were almost the same as those for SC-FF1. Fig. 7 provides a comparison of the SEM photos of the zeolite A particles synthesized from these two synthesis cakes at 70 ^oC and 90 ^oC. The particles obtained from SC-FF1 were smaller than those from SC-FF2, while the particles obtained at 70 ^oC were also smaller than those at 90 ^oC from both the cakes, indicating that further nucleation occurred during the hydrothermal reaction in both cases. The zeolite A synthesized from SC-FF2 at 90 ^oC was comprised of uniform cubic particles with the largest size of about 1 μm. This was attributed to the rapid crystallization at the higher temperature, and the suppression of further nucleation during the hydrothermal reaction due to the lowered alkalinity. The XRD patterns of the particles shown in Fig. S7 were indistinguishable from those of SC-SF shown in Fig. 1, indicating that crystallization from synthesis cakes is indeed suitable for the large-scale production of zeolite A without sacrificing product quality in terms of crystallinity and particle size. The lowering of alkalinity in the synthesis cakes helps to control the quality of the zeolite A product obtained.

The most important aspect of the crystallization of zeolite A from the synthesis cake prepared using a filter press is the reduction of reactant volume to one-eighth and the reactant weight to one-fourth. The shrunken reaction volume directly reduces the reactor volume required for the subsequent hydrothermal reaction by the same factor. Considering that the highly alkaline synthesis mixture (pH > 14) necessitates the use of a very expensive Teflon-coated reactor, the smaller reactor volume will significantly lower the capital cost. Since zeolites produced are recovered by filtering from the products of hydrothermal reaction in the conventional process, the filter pressing of synthesis mixtures before hydrothermal reaction in the suggested process does not require any additional equipment and operation cost. According to the cost estimation carried out by Biniwale el al. in the paper entitled “Cost estimates for production of flyash based zeolite-A,” the reactor occupied 47% of the total capital cost required for 7,500kg/d production of zeolite A.[26] This percentage would rise to 66% for a zeolite synthesis process using conventional raw materials if the cost for the ball-mill and furnace installed for the crushing and calcination of flyash were excluded from the total cost. Thus, the crystallization from synthesis cake is expected to more than halve the capital cost required in comparison to use of a synthesis mixture. Furthermore, the energy cost for hydrothermal reaction can be reduced to a quarter, corresponding to the weight reduction factor.

The proposed method for synthesizing zeolite A from synthesis cake fulfills the conditions for an eco-friendly process: drastic lowering of the installation cost, and considerable energy saving without sacrifice of the product quality in terms of crystallinity and particle size distribution. The same approach can be applied to the production of zeolites with various frameworks, such as ANA, GIS, FAU, MFI, and BEA, which will be pursued in our future research.

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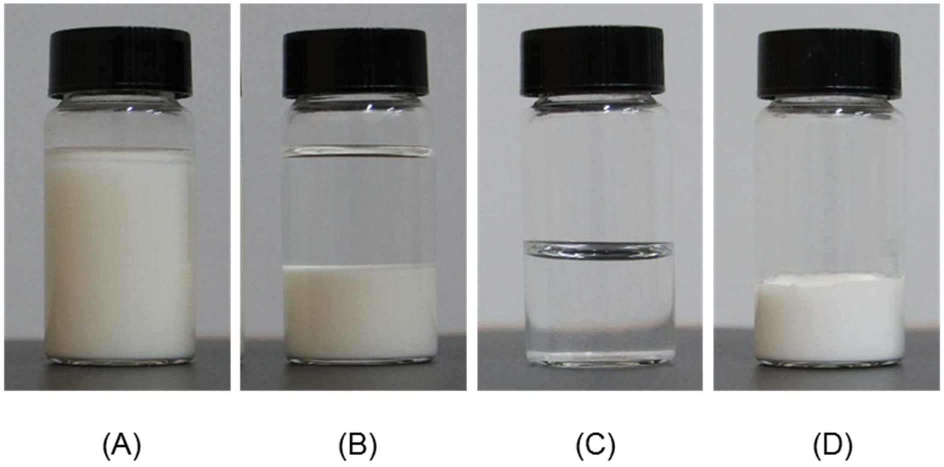


Fig. 1. Photos of synthesis mixture and cake in the synthesis of zeolite A: Synthesis mixtures (A) as prepared, (B) after ageing, (C) removed liquid phase, and (D) prepared synthesis cake by simple filtering.

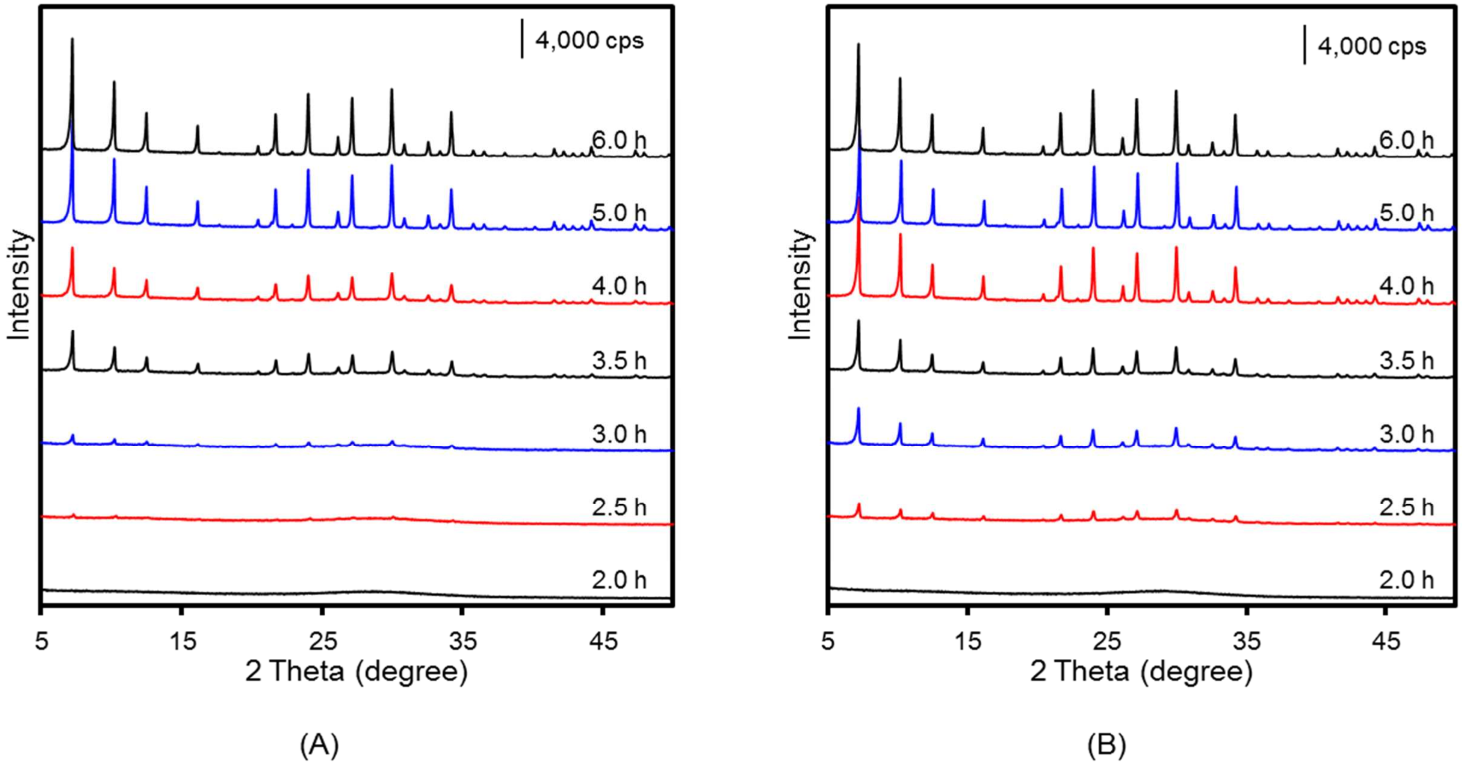


Fig. 2. XRD patterns of solid phases obtained in the crystallization of zeolite A from (A) SM-SF and (B) SC-SF at 70 ºC.

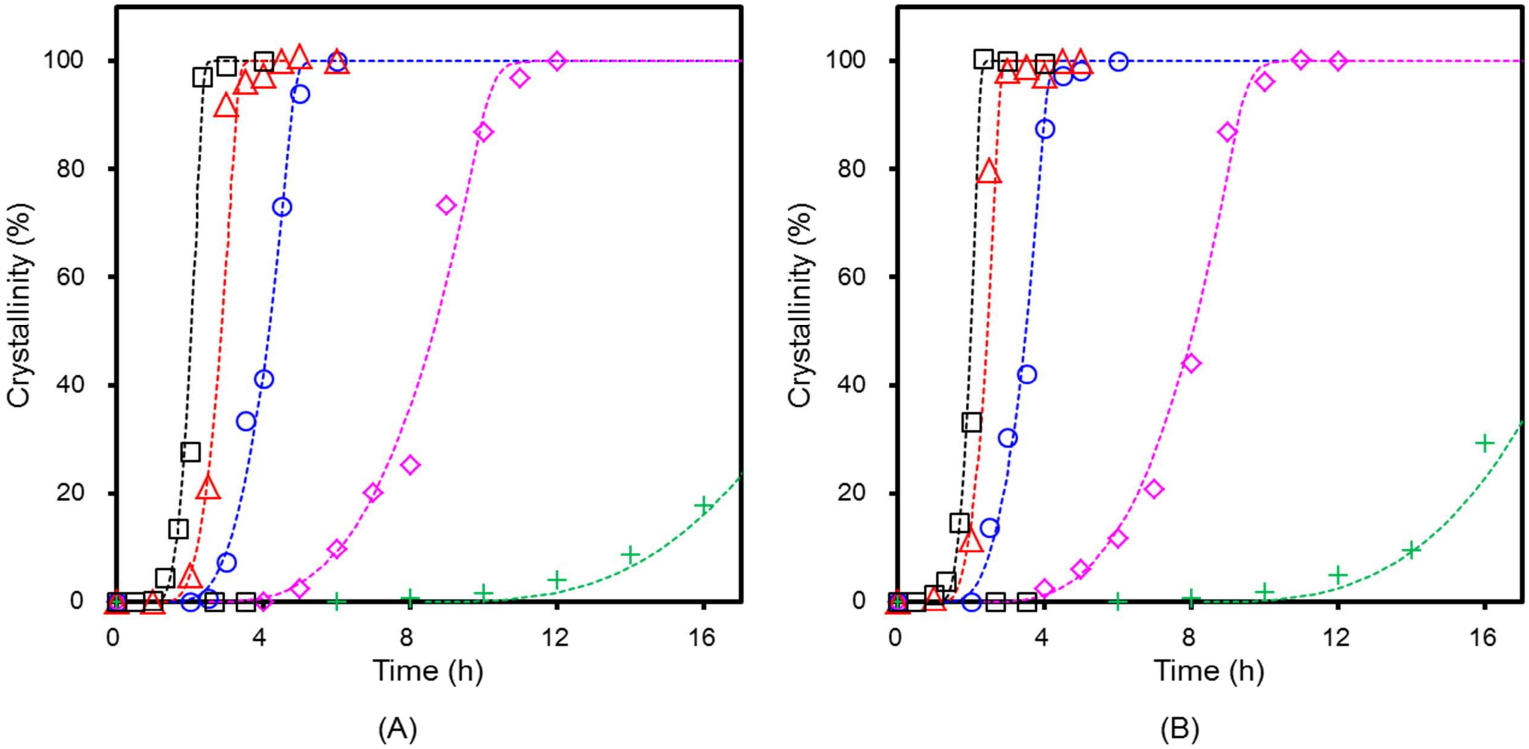


Fig. 3. Crystallization curves of zeolite A in the hydrothermal reaction of (A) SM-SF and (B) SC-SF at different temperatures: (+) 50 ºC, (♢) 60 ºC, (○) 70 ºC, (Δ) 80 ºC and (□) 90 ºC.

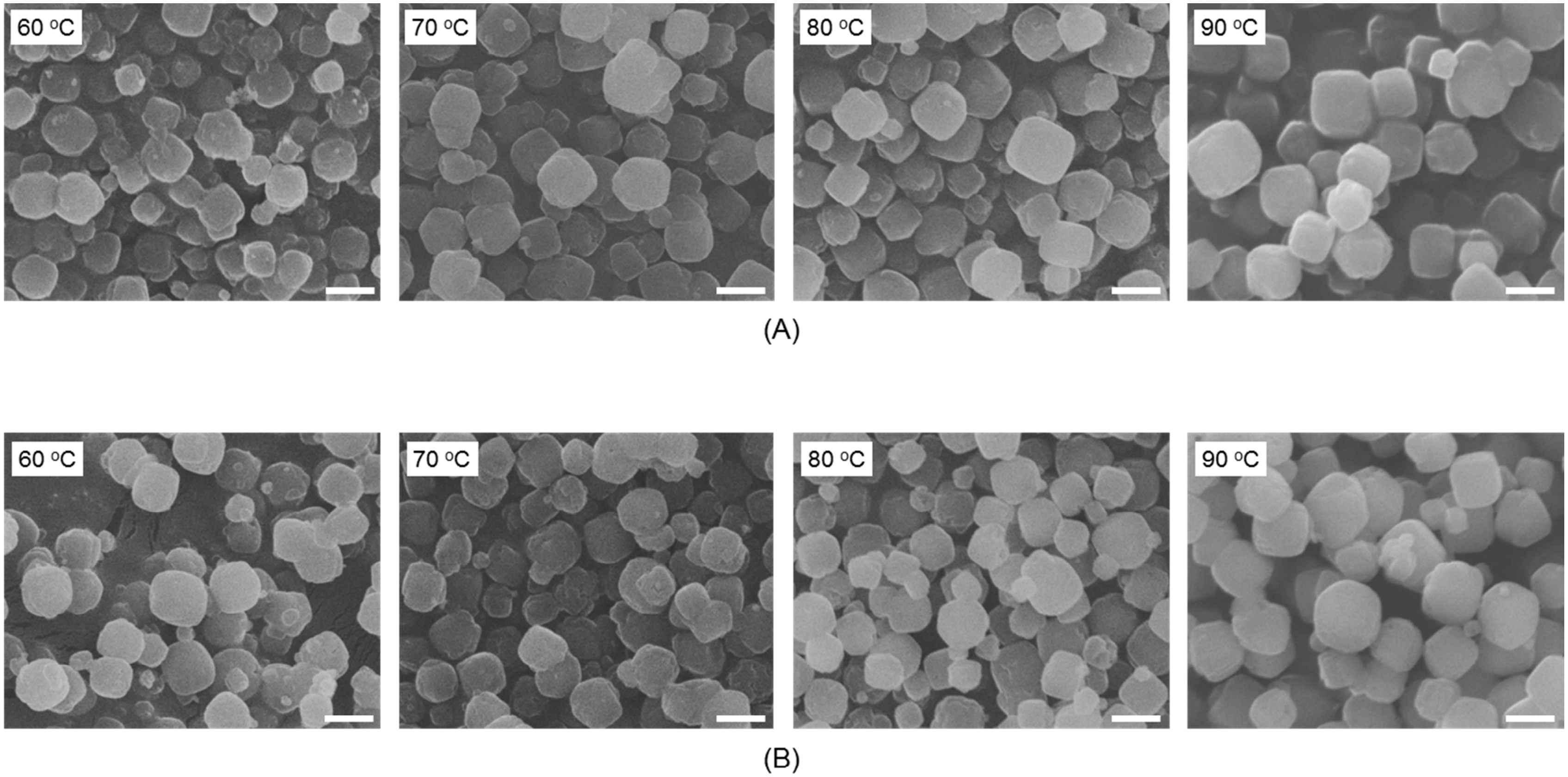


Fig. 4. SEM photos of zeolite A synthesized by hydrothermal reaction of (A) SM-SF and (B) SC-SF at different temperatures. Reaction time was varied with temperature: 12 h at 60 °C, 6 h at 70 °C, 4 h at 80 °C, and 3 h at 90 °C. The inserted scale bars represent 1.0 μm.

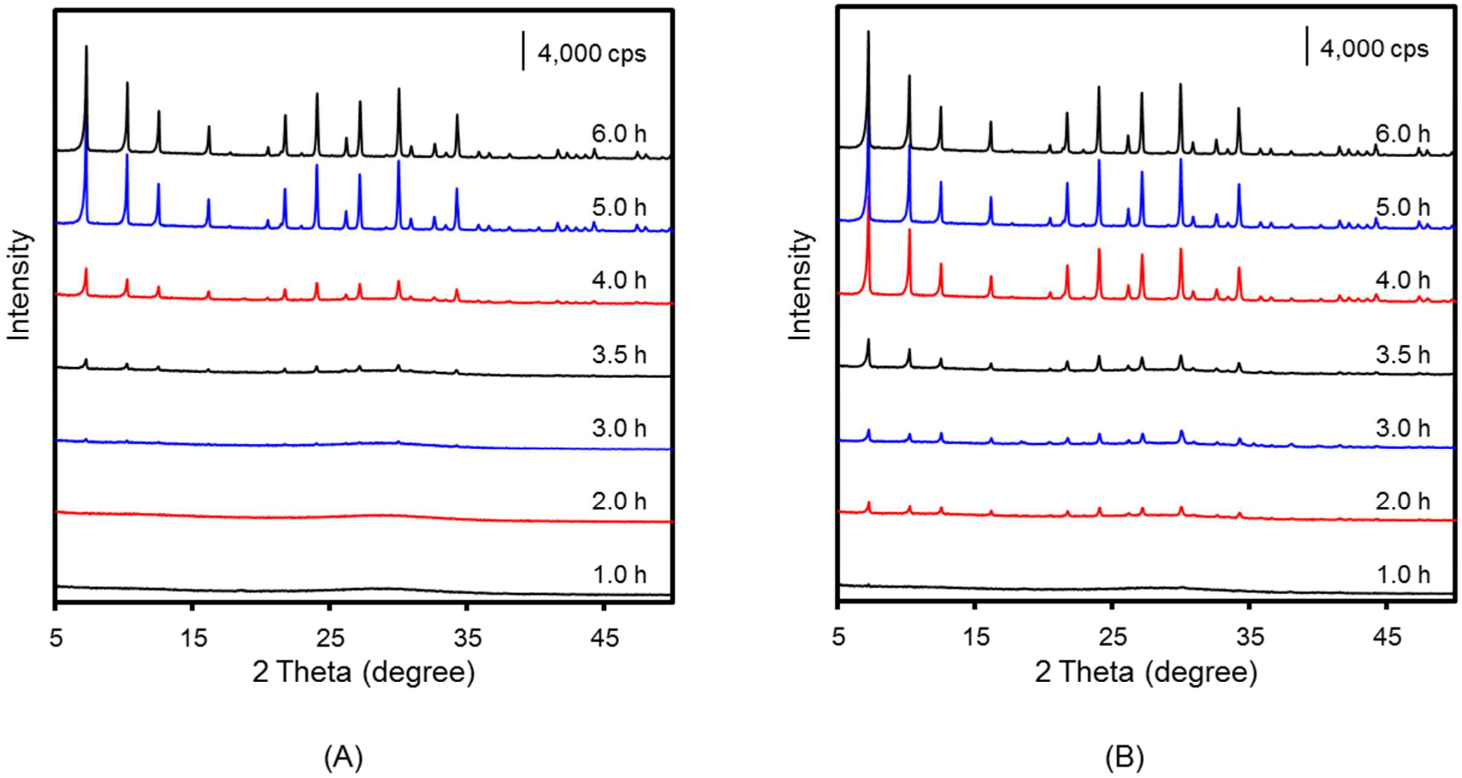


Fig. 5. XRD patterns of solid phases obtained in the crystallization of zeolite A from (A) SM-HC and (B) SC-HC at 70 °C for different reaction times.

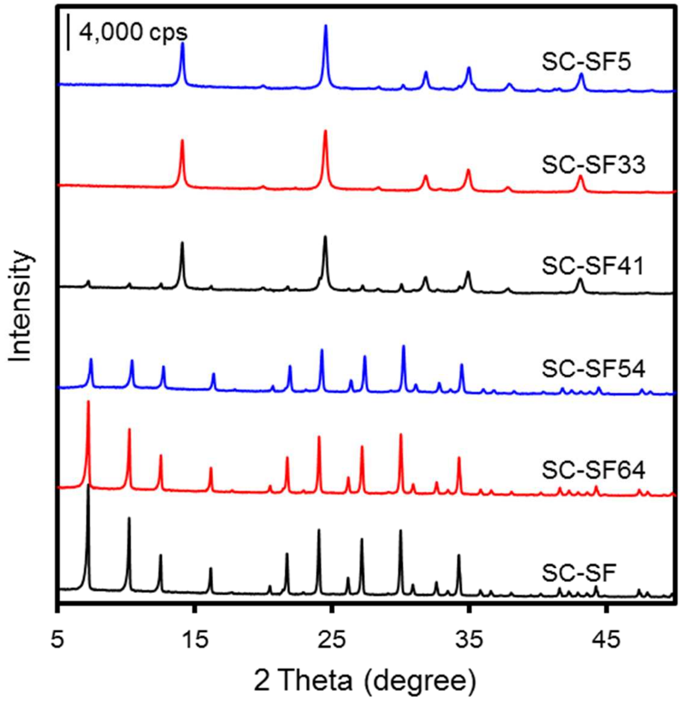


Fig. 6. XRD patterns of zeolite A obtained from SC-SF with different water contents through hydrothermal reaction of at 70 °C for 9 h.

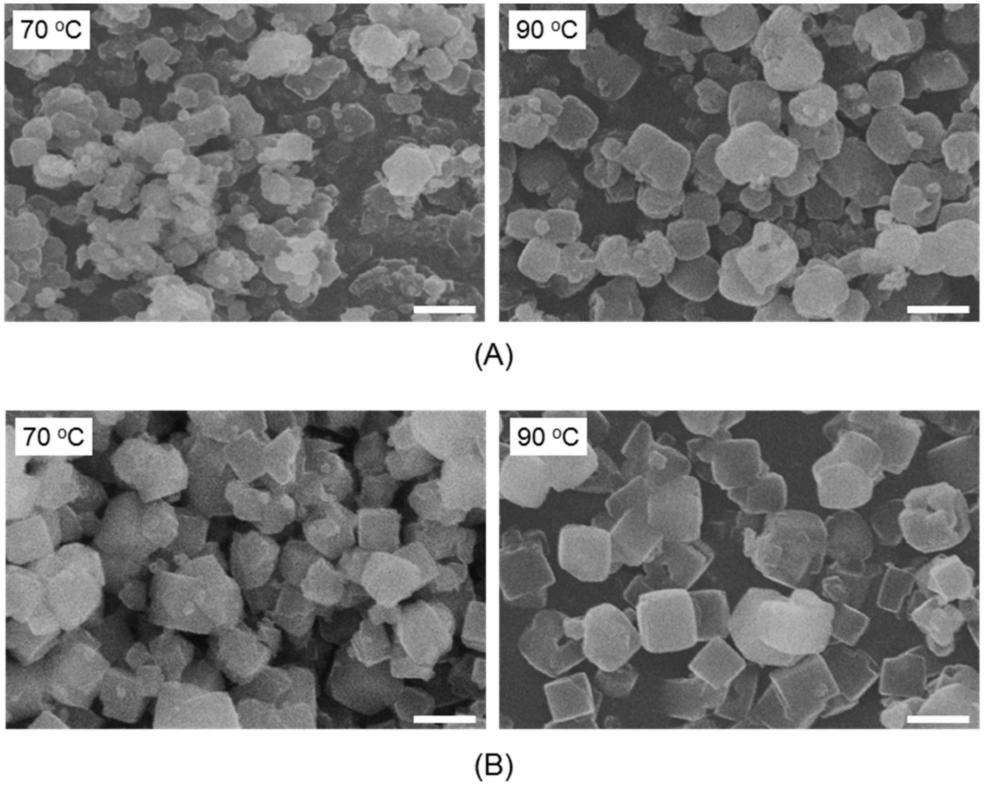
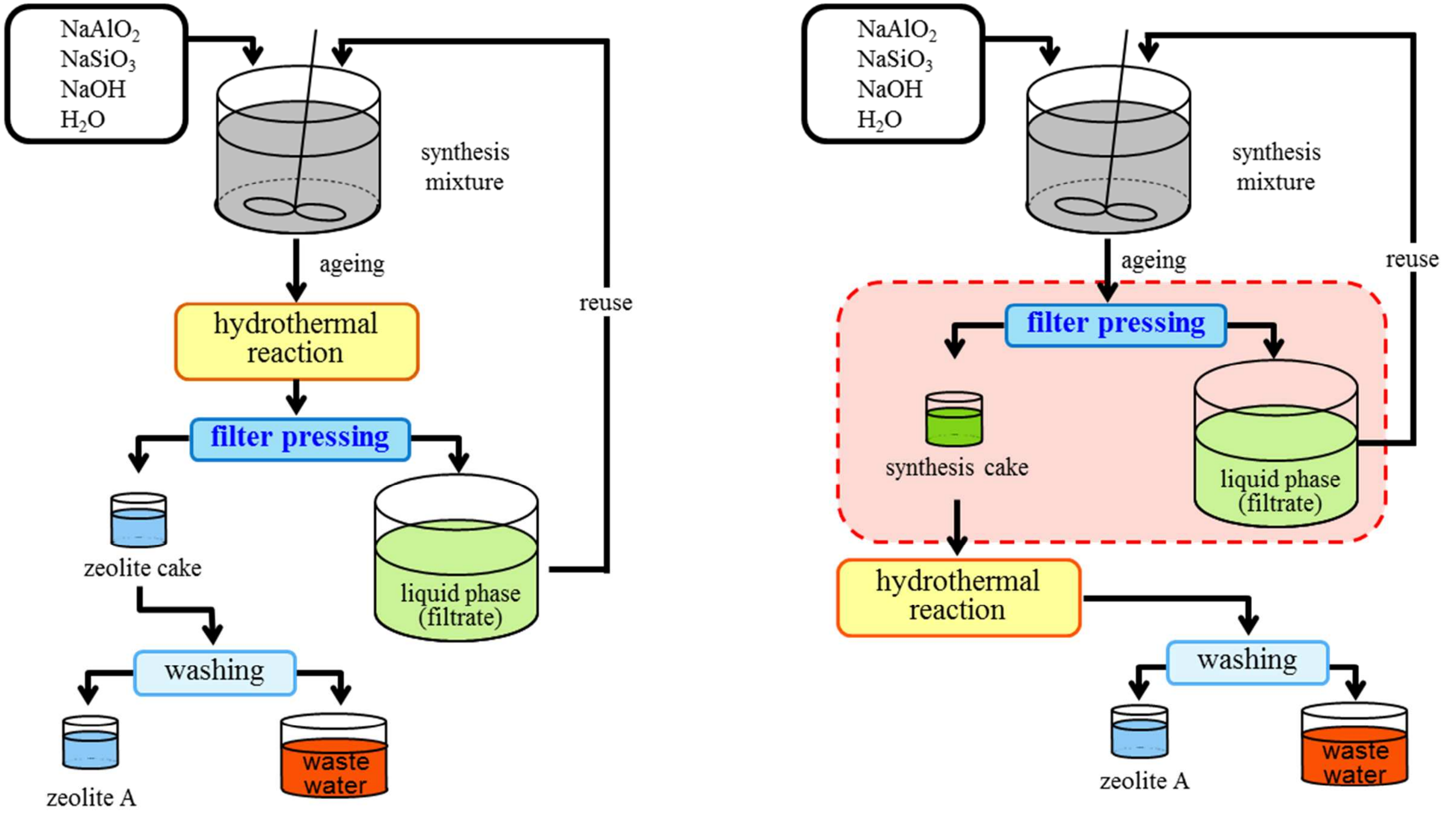


Fig. 7. SEM photos of zeolite A synthesized by hydrothermal reaction of (A) SC-FF1 and (B) SC-FF2 at 70 °C for 6 h and 90 °C for 5 h. The inserted scale bars represent 1.0 μm.



Conventional process

Eco-friendly process

Scheme 1. Comparison between the conventional and eco-friendly processes for the synthesis of zeolite A.

Table 1. The adjusted parameters for the best fits for the crystallization curves of zeolite A

Temperature (°C)	Starting material							
	SM-SF				SC-SF			
	Average particle size (µm)	t_{ind} (min)	k_{grow} (µm min^{-1})	E_a (kJ mol^{-1})	Average particle size (µm)	t_{ind} (min)	k_{grow} (µm min^{-1})	E_a (kJ mol^{-1})
50	-[a]	304	0.052	79	-	336	0.060	66
60	0.67	175	0.14		0.75	124	0.13	
70	0.82	109	0.35		0.81	48	0.29	
80	0.84	87	0.61		0.83	42	0.47	
90	1.10	49	0.62		1.01	34	0.47	

[a] the crystallization at 50 °C was not completed even after reaction for 24 h.