

Semiflow Microwave Heating Reactor with Resonator Moving Mechanism Applied to Zeolite Synthesis

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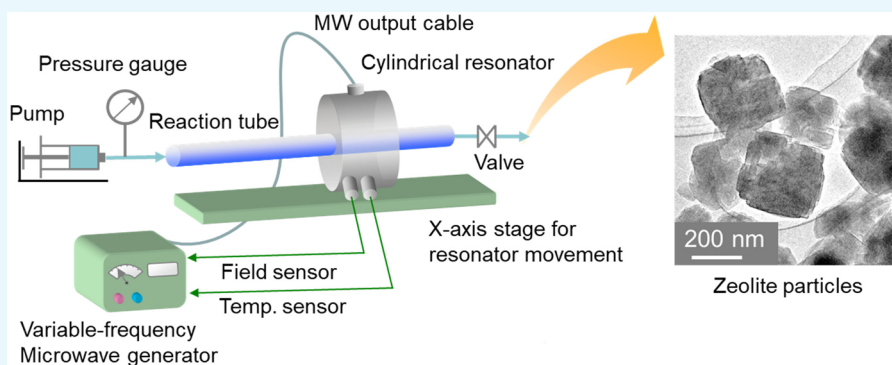
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ABSTRACT: A semiflow microwave (MW) heating reactor similar to a flow reactor system was developed. Slurry raw materials in the reaction tube were heated continuously and cooled rapidly by moving a thin MW resonator instead of flowing slurry raw materials. From highly viscous mother slurries, Linde-type A (LTA) and faujasite (FAU)-type zeolite nanoparticles of small crystal grains were synthesized quickly. Results show that this heating system can synthesize hydroxy-sodalite (SOD)-type zeolite from coal fly ash particles including those larger than 50 μm . Numerical calculations using the COMSOL Multiphysics program revealed the thermal distribution of liquids of various viscosities using the semiflow MW heating reactor.

INTRODUCTION

A transition from batch-type to flow-type production processing is underway in various industrial fields.^{1–11} Flow-type processing reduces the need for separation and purification of intermediate products and enables continuous processing from raw material supplies to the final product. Flow processes are being put to practical use in the fields of petrochemicals, fine chemicals, and pharmaceutical manufacturing, which are also contributing to energy cost reduction and environmental load reduction.^{12–14}

Microwave (MW) heating, which enables direct and selective heating of materials, is an effective heat source for constructing efficient production processes.^{15–18} However, using conventional MW equipment, which requires a magnetron generator, uniform MW irradiation is difficult to provide because of the output fluctuation.^{19,20} Therefore, batch-type equipment with a stirring mechanism is mainly used. In recent years, the adoption of a semiconductor-type MW generator has enabled accurate irradiation in a narrow wavelength band in addition to the reduction of output fluctuations.²⁰ The development of new MW equipment, including flow-type processing, is progressing rapidly.^{21–29}

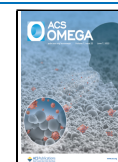
For the past 10 years, we have also developed a flow-type MW heating reactor with a cylindrical resonator.^{21,23} Its salient

feature is that uniform MW irradiation can be maintained by constantly feeding back the resonance frequency, which varies depending on the internal state to the oscillation frequency using a variable-frequency semiconductor generator. With this mechanism, a stable electromagnetic field distribution is always maintained on the central axis of the cylindrical resonator, where the reaction tube is installed. Various metal nanoparticle syntheses and catalytic reactions were also performed using this reactor.^{25,30,31} Moreover, we have developed another type of flow process: sheet-type flow processing.³² It is effective for reactions involving highly viscous raw material solutions and raw materials that generate gas, which are difficult to handle with conventional flow processes that use reaction tubes. For this process, the raw material solution is held by the capillary phenomenon between the sheet fibers. Then, MW heating was conducted while transporting the raw material solution,

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similarly to a belt conveyor; an example of its application to metal nanoparticle synthesis was presented.

Other examples that are difficult to handle with flow processes include reactions using slurry under pressure, which requires a closed system. Slurry raw materials present a risk of clogging in the liquid feed pump and the pressure-reduction valve. One example is zeolite particle synthesis. Zeolites, which are porous oxide crystals made of silica and alumina, are widely used industrially as separation/adsorbents, catalysts, etc.^{33–35} In recent years, zeolite syntheses in flow processes have been studied actively while undertaking various efforts such as fluid control using droplet formation or mixing control with a micromixer.^{36–39} Few reports have described flow-MW zeolite synthesis that is able to produce high yields.^{40,41}

As presented herein, we developed a semiflow MW heating reactor for syntheses using slurry raw materials in closed systems that require pressurization. This reactor was designed so that flow-type reactors with rapid homogeneous heating and cooling are producible by moving a thin cylindrical resonator using a reaction tube similarly to the flow process. We demonstrated the syntheses of LTA-type and FAU-type zeolite particles. In addition, zeolite synthesis from coal fly ash was performed as a synthetic example including larger particles (approximately 50 μm). Furthermore, numerical calculations using the COMSOL Multiphysics program revealed the thermal distributions in the reaction tube using a semiflow reactor. By comparing the simulations of MW heating and conventional heating for various viscosity liquids, the heat transfer characteristics of this semiflow reactor were ascertained.

EXPERIMENTAL SECTION

Semiflow MW Reactor. Figure 1 presents a schematic drawing and the appearance of the semiflow MW reactor. This

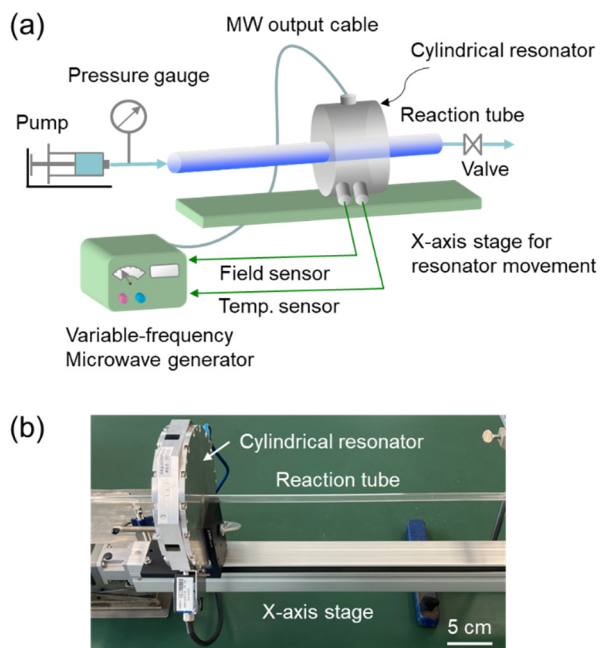


Figure 1. (a) Schematic drawing and (b) appearance of the semiflow MW reactor. In this reactor, after the reaction tube is filled with the raw material slurry to stop the flow, the reaction tube is heated continuously by moving the resonator. Finally, the reactant is discharged after the heating is completed. This cycle is repeated.

reactor consists mainly of a cylindrical resonator with a moving mechanism, a variable-frequency semiconductor generator (2.4–2.5 GHz, 0–100 W), and a liquid transfer unit.^{23,42} The resonator's inner diameter is designed so that the electromagnetic field distribution on the central axis of the resonator is maximized. The reaction tube is installed on the central axis. By feeding back the resonance frequency reflecting the inner state in the reaction tube to the oscillation frequency, a homogeneous electromagnetic field distribution is always formed. In this semiflow reactor, the reaction tube liquid does not flow during MW heating; instead, the resonator moves. In fact, the resonator was moved with an X-axis stage (300 mm movable distance) controlled using a servo motor. As a synthetic procedure, the raw material slurry is first filled in the reaction tube with a syringe pump. Subsequently, continuous MW heating is performed while moving the thin (20 mm) resonator. After MW heating is completed, the ball valve on the discharge side is opened. Then, the reaction product is discharged while the next raw material slurry is pumped and the resonator is returned to the start position. This cycle is repeated. By alternating the transfer of the slurry and the MW heating, one can avoid clogging in the pump and in the back pressure valve, which tend to occur during flow syntheses. During zeolite synthesis, the magnetic field concentrated TM₁₁₀ mode was used instead of the commonly used electric field concentrated mode. In our earlier studies, TM₁₁₀ mode MW heating was suitable for highly conductive liquids such as zeolite raw materials.^{32,40} The reaction tube temperature was measured using a radiation thermometer (TMHX-CNE500-0070E003; Japansensor Corp.) with 0–500 °C measurable range. The measurement wavelength is 2–6.8 μm , which is the wavelength range that permeates partially through quartz.

Synthetic Conditions of Zeolite Particles. Similarly to our earlier study,⁴⁰ the raw material slurry for LTA-type zeolite synthesis can be described as follows: each of 30% colloidal silica, sodium hydroxide, and sodium aluminate was dissolved in distilled water and mixed in the molar ratios of Na/Al/Si/H₂O = 4:1:1:53. After stirring at room temperature for 24 h, the slurry was supplied to a quartz reaction tube (ID 4 mm, OD 6 mm) and was heated continuously in the magnetic field by moving a 2.45 GHz cylindrical resonator (146 mm diameter; 20 mm width) at 1 mm/s (equivalent to heating time of 20 s). The reaction tube temperature during the MW irradiation was controlled to 140 °C. The internal pressure was controlled to around 0.8 MPa. The product was collected by centrifugation and was washed with pure water several times by centrifugation. Subsequently, the precipitate was dried at room temperature. Particle analysis was performed. In addition, to confirm the slurry temperature, an experiment comparing the surface temperature of the reaction tube with the internal temperature was conducted under MW heating at atmospheric pressure. An optical fiber thermometer (FL-2000; Anritsu Meter Co., Ltd.) was installed in the reaction tube. The temperature findings were compared with those obtained from the radiation thermometer. Furthermore, to compare the particle size distribution, LTA-type zeolite synthesis was performed using flow-type MW heating (140 °C, 2 min), batch-type MW heating (140 °C, 2 min), and conventional heating (140 °C, 1 h) on the basis of the synthetic conditions used for our earlier study.⁴⁰

The raw material slurry for FAU-type zeolite synthesis is described as follows: each of 30% colloidal silica, sodium hydroxide, and sodium aluminate was dissolved in distilled

water and was mixed at molar ratios of Na/Al/Si/H₂O = 4:1:1:90. After stirring at room temperature for 240 h similarly to our earlier work,⁴³ the slurry was supplied to a quartz reaction tube and was heated continuously in the magnetic field by moving a cylindrical resonator at 10 mm/min (2 min heating time). The reaction tube temperature was controlled at 140 °C during MW irradiation. The internal pressure was controlled around 0.8 MPa. Then, centrifugation and drying were performed.

The raw material slurry including coal fly ash is described as follows: after 5 M aqueous sodium hydroxide solution was added to coal fly ash (JIS standard type IV), the mixture was stirred at room temperature for 10 min. The amount of coal fly ash contained in the raw material slurry was about 35 wt %. The speed of the resonator motion was 2 mm/min (10 min heating time). The reaction tube temperature during MW irradiation was controlled at 140 °C; the internal pressure was controlled to around 0.8 MPa. Then, centrifugation and drying were performed.

Analyses of Semiflow Synthesized Zeolite Particles. An X-ray diffractometer (XRD, SmartLab; Rigaku Corp.) was used for structural analyses. Dynamic light scattering spectroscopy (DLS, ELS-Z; Otsuka Electronics Co., Ltd.), scanning electron microscopy (SEM, S-4800; Hitachi High-Technologies Corp.), and transmission electron microscopy (TEM, TECNAI G2; FEI Co.) were used to analyze the particle size and shape. The water vapor adsorption isotherm and the nitrogen adsorption isotherm were obtained, respectively, from the following apparatus: BELSORP-aqua3 and BELSORP MAX (MicrotracBEL Corp.). Mercury porosimetry (Autopore 9500; Micromeritics Instrument Corp.) was conducted to analyze the size distribution of mesopores and macropores in the LTA-type zeolite sample. In addition, a sine-wave vibro viscometer (SV-10A; A&D Co. Ltd.) was used to measure the LTA-type raw material slurry viscosity.

Thermal Distribution of Semiflow Reactor Obtained by Numerical Calculation. The thermal distribution of the liquid that absorbed the electromagnetic energy supplied by the moving resonator was obtained using a finite element method simulation conducted using the COMSOL Multiphysics program.⁴⁴ On the basis of the heat transfer and fluid governing equations, numerical calculations were performed using a model that incorporated heat convection using a radiofrequency module, a heat transfer module, and a CFD module. Moreover, by moving the heating zone over time and by performing calculations, the temperature distribution in the reaction tube was estimated over time. In addition to MW heating, the temperature distribution under conventional heating was calculated. In MW heating, the entire liquid in the resonator generates heat. However, during conventional heating, heat flows from the outer wall of the reaction tube with an electric furnace having the same width as the MW resonator. The dielectric loss coefficient of the liquid used the value of water (10 at 25 °C). Details of the parameter values used for numerical calculations such as the reaction tube size are presented in Table 1.

RESULTS AND DISCUSSION

LTA-Type Zeolite Synthesis Using Semiflow MW Reactor. For the LTA-type zeolite synthesis, the reaction tube was filled with the raw material slurry (Na/Al/Si/H₂O = 4:1:1:53). Semiflow MW synthesis (140 °C, 20 s) was performed while moving the resonator. The reactor surface

Table 1. Details of Parameter Values Used for Numerical Calculations

parameter	set values
MW power or electric furnace power	10 W
viscosity of liquid	1, 10, 100 mPa·s
resonator width	20 mm
resonator moving speed	1 mm/s
quartz reaction tube inner diameter	4 mm
quartz reaction tube outer diameter	6 mm
reaction tube length	150 mm

temperature was maintained at 140 ± 5 °C during MW heating. It has been pointed out that the surface temperature of the reaction tube and the internal temperature differ under MW heating.⁴⁵ In the experiment conducted at atmospheric pressure, when the slurry temperature inside the reaction tube measured by the optical fiber thermometer was 100 °C, the radiation temperature on the reaction tube surface was 97–98 °C. Therefore, the slurry temperature was estimated as about 5–10 °C higher when the reaction tube outer wall temperature was 140 °C.

The slurry after MW heating appeared to have solid–liquid separation. Single-phase LTA-type structure was confirmed from the XRD pattern of the synthetic sample presented in Figure 2a. Homogeneous particles with approximately 400 nm particle diameter were observed in the SEM image (Figure 2b). In our earlier study of flow MW synthesis, homogeneous particles with approximately 400 nm particle diameter were observed.⁴⁰ Also, 500–1000 nm particles were obtained from batch MW heating and conventional heating.⁴⁰ Even in the particle size distribution obtained from DLS, the particles synthesized by flow and semiflow MW heating were smaller than the particles synthesized by batch MW and conventional heating (Figure 2c). During the particle synthesis process, rapid and homogeneous heating by MW caused more nucleation than conventional heating.³⁴ Subsequently, because it was cooled rapidly after maintaining a uniform heating field in the flow and semiflow MW heating synthesis, it was presumed that the dissolution of microcrystals and the regrowth of particles because of Ostwald ripening were suppressed.⁴⁰ Consequently, LTA-type zeolite particles having smaller particle size were obtained from semiflow synthesis as well as from flow MW synthesis. Additionally, heating times of several minutes to several tens of minutes are necessary for batch MW heating and conventional heating. Therefore, this reactor can synthesize LTA-type zeolite particles during the short time of 20 s. In the TEM image, many small grains were observed on the inner side of the rigid cubic-shaped particles on the outside (Figure 2d). Furthermore, the small grain size was similar to that of crystal grains of the mesoporous LTA-type zeolite reported earlier from flow synthesis.⁴⁰ Pore size data obtained using a mercury porosimeter indicated that mesopores and macropores were formed in addition to the micropores (Figure 2e). The water vapor adsorption isotherm confirmed that, in addition to water adsorption by micropores with RH of less than 20%, water adsorption also presented in the mesopore region with RH of 20% or more (Figure 2f). The description above revealed that LTA-type zeolites having similar features to those synthesized in the flow system are obtainable in the semiflow system. From these experiment results, one syringe pump was used. After MW heating, the synthetic sample was extruded by supplying a raw material

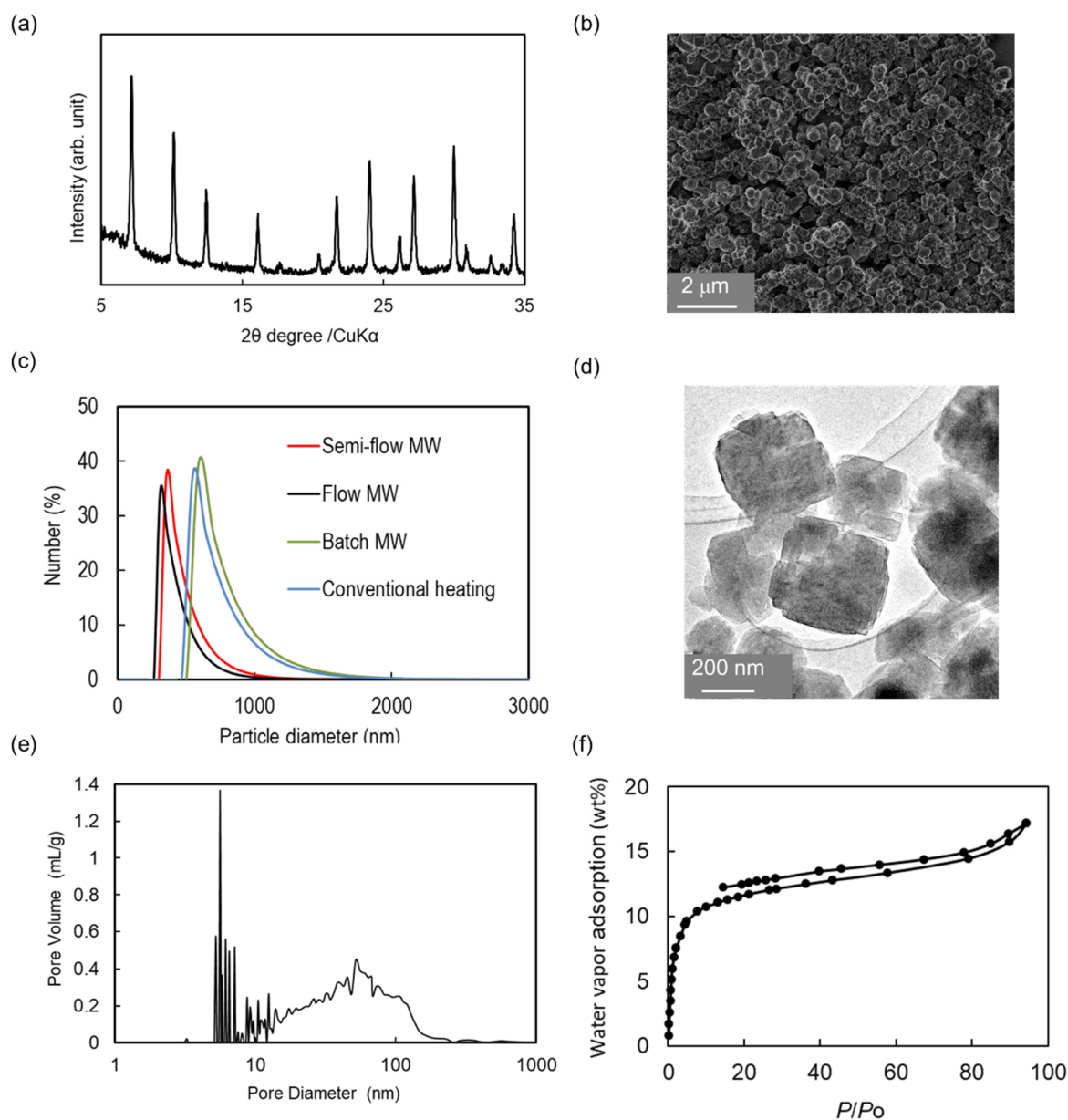


Figure 2. (a) XRD pattern, (b) SEM image, (c) particle size distribution obtained by DLS, (d) TEM image, (e) pore size distribution measured using a mercury porosimeter, and (f) water vapor adsorption isotherm for semiflow MW synthesized LTA-type zeolite. The raw material solution, which is $\text{Na}/\text{Al}/\text{Si}/\text{H}_2\text{O} = 4:1:1:53$, was stirred at room temperature for 24 h.

slurry in an amount slightly smaller than the volume of the reaction tube. Therefore, it is presumed that a synthetic sample with a longer heating time was mixed. By supplying and discharging the slurry using separate pumps, higher-quality synthesis can be achieved. In this reactor system, the semiflow synthesis cycle can be conducted continuously and repeatedly using a double piston pump.

Nanosized FAU-Type Zeolite Synthesis Using a Semiflow MW Reactor. Subsequently, semiflow MW synthesis of FAU-type zeolite was conducted under conditions similar to those used for LTA-type zeolite synthesis except that the raw material slurry, aging time, and MW heating time differed. The reaction tube was filled with the raw material slurry ($\text{Na}/\text{Al}/\text{Si}/\text{H}_2\text{O} = 4:1:1:90$, stirred at room temperature for 240 h). Semiflow MW synthesis ($140\text{ }^\circ\text{C}$, 120 s) was performed. The FAU-type zeolite single phase was confirmed from the XRD pattern (Figure 3a). From the TEM images

presented in Figure 3b,c, the formation of crystal particles having 10–30 nm particle diameter was confirmed. The lattice fringe shows that each nanoparticle was well-crystallized. Nitrogen adsorption measurements were taken to investigate the pore characteristics. Pore volumes in the micropore ($P/P_0 \leq 0.1$), mesopore ($0.1 < P/P_0 \leq 0.96$), and macropore regions ($0.96 < P/P_0 \leq 0.99$) were, respectively, 0.24, 0.54, and 0.50 cm^3/g . The Brunauer–Emmett–Teller (BET) surface area was $670\text{ m}^2/\text{g}$ (Figure 3d). Furthermore, the pore size distribution of the mesopore calculated using the BJH method is shown in Figure 3e. A broad peak visible at around 44 nm is probably attributable to interstices among the nanoparticles. Reportedly, homogeneous microcrystal nuclei were generated by aging treatment of the raw material slurry. Nanosized FAU-type zeolites having 10–15 nm particle size were synthesized.⁴⁶ Semiflow MW synthesized particles had a greater specific surface area than the earlier report value of $180\text{ m}^2/\text{g}$,⁴⁶ which

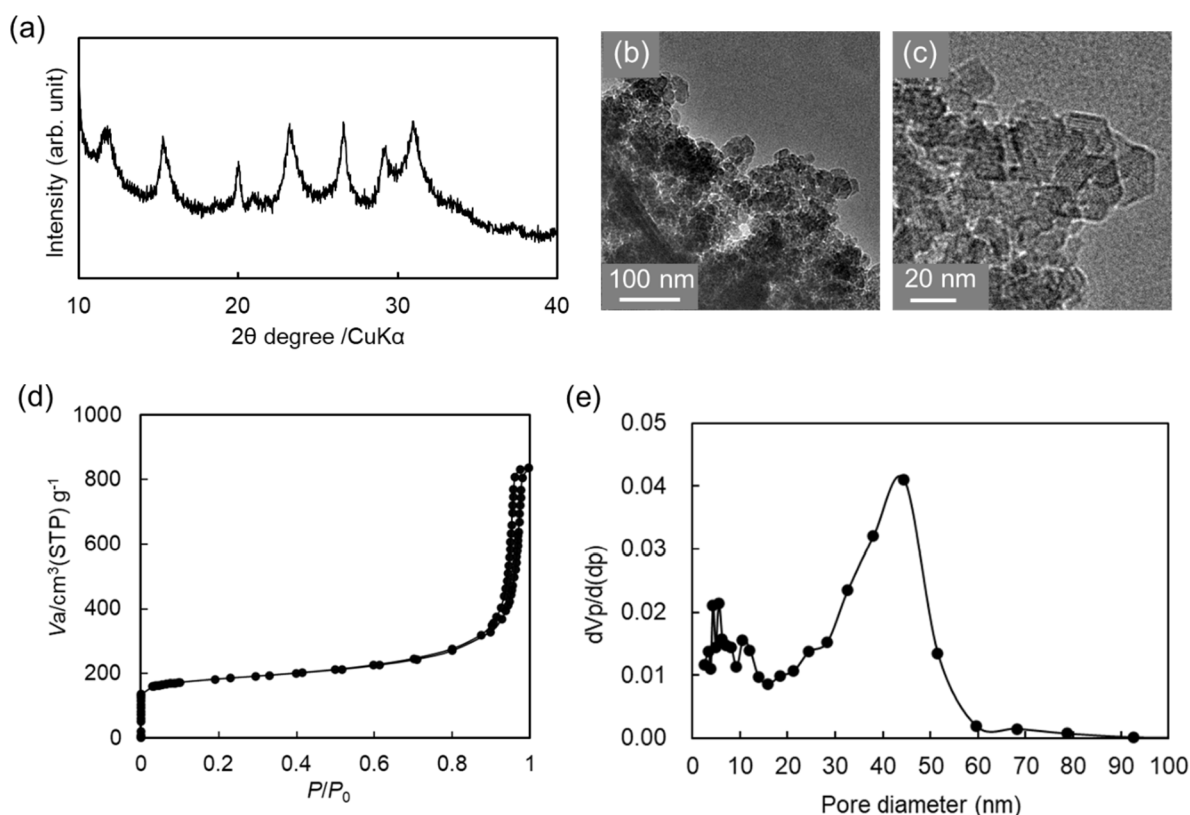


Figure 3. (a) XRD pattern, (b and c) TEM images, (d) nitrogen adsorption isotherm, and (e) pore size distribution of the mesopore by the BJH method for semiflow MW synthesized FAU-type zeolite. The raw material solution is Na/Al/Si/H₂O = 4:1:1:90, which was stirred at room temperature for 240 h.

suggests that this semiflow heating system formed fine homogeneous particles including less-amorphous particles. The discussion presented above showed that the semiflow MW heating system presents benefits for nanosized zeolite synthesis with large specific surface area.

Zeolite Synthesis from Coal Fly Ash Using a Semiflow MW Reactor. For synthesis from raw materials containing large particles (approximately 50 μm), slurry transfer becomes difficult because of sedimentation, which makes flow synthesis even more difficult. Semiflow synthesis of zeolite from coal fly ash was conducted as an illustrative example. Zeolite synthesis using coal fly ash can be performed in tens of minutes to several hours when using MW heating, whereas conventional heating requires several hours to several tens of hours. Therefore, it has been studied actively using MW heating in recent years.⁴⁷ Sodium hydroxide aqueous slurry including coal fly ash was filled in a reaction tube. Then semiflow MW synthesis was conducted at 140 °C for 10 min. Figure 4a shows the XRD patterns obtained for coal fly ash particles before and after MW heating. After MW heating, in addition to the peaks of quartz and mullite contained in the raw materials, which were mixtures confirmed in the earlier study,⁴⁸ SOD-type zeolite peaks were confirmed. The SEM images presented in Figure 4b,c show that the surface areas of particles were greater after MW heating because of undulations on the particle surface. In this synthesis, sedimentation of the particles was observed during MW heating. For maintaining a homogeneous slurry state, one must take measures such as vibrating of the reactor tube, as reported in the literature.⁴⁹ However, this reactor can shorten the synthesis time. Therefore, it is valuable

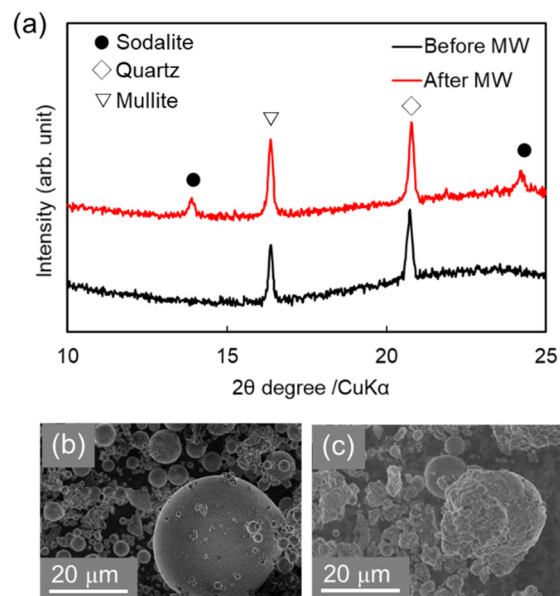


Figure 4. (a) XRD pattern and (b and c) SEM images of coal fly ash particles before and after semiflow MW heating.

for synthesis with a raw material slurry that is prone to precipitate.

Thermal Distribution of Semiflow MW Heating Reactor Obtained by Numerical Calculations. Numerical calculations were performed to obtain general insight into the heating characteristics of the semiflow MW reactor. First, we compared the heat distribution of a liquid in the reaction tube

with and without consideration of heat convection. We also compared it with conventional heating (CH), by which heat flows in from the outer wall of the reaction tube. Parts a and b of Figure 5 show the thermal distribution obtained when a

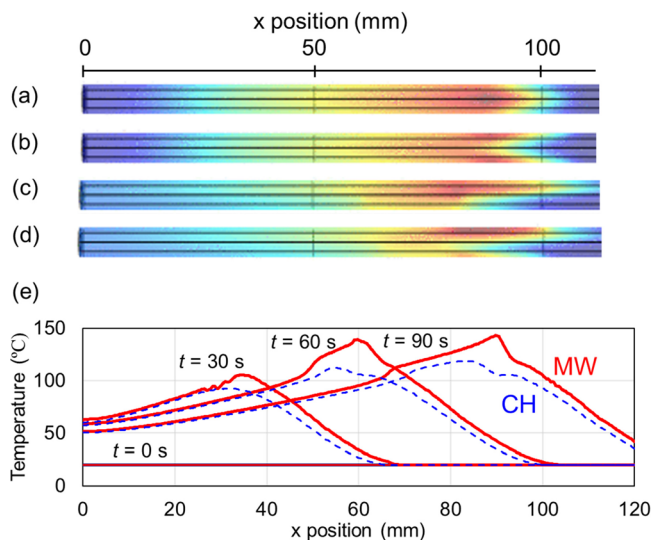


Figure 5. Thermal distribution of semiflow reactor when the resonator moves from 0 to 90 mm: (a) MW heating and (b) conventional heating (CH) without considering heat convection, (c) MW heating, and (d) CH considering heat convection. (e) Heat distribution in the reaction tube considering heat convection by MW heating and CH. The displayed time is the elapsed time from the start of heating. The liquid viscosity was calculated as 1 mPa·s.

liquid with a viscosity of 1 mPa·s, which is equivalent to pure water, is heated while moving the resonator to a 0–90 mm position without consideration of heat convection. In MW heating, the temperature of the central part in the reaction tube became high. In CH, the temperature near the outer wall became high. The central part of the reaction tube tended to be heated with a delay. Considering heat convection, the upper side of the central axis of the reaction tube was heated easily by MW heating, presuming that ascending flow was generated (Figure 5c). In CH, the central part of the reaction tube tended to be difficult to heat (Figure 5d). Figure 5e shows the temperature distribution at the central axis of the reaction tube after heating as 0–90 s. Actually, MW heating shows a steeper curve than CH. These findings confirmed that the temperature of the narrow area in the reaction tube rises sharply. Next, we investigated the liquid viscosity effects on the heat distribution. Parts a–c of Figure 6 show the thermal distribution by MW heating calculated at viscosities of 1, 10, and 100 mPa·s. Parts d–f of Figure 6 show the thermal distribution by CH calculated using the same viscosities. Higher viscosities are associated with less ascending flow and greater uniform thermal distribution. Furthermore, its characteristics were clearer for MW heating than for CH. The results presented above clarified that more homogeneous MW heating can be achieved using a reaction tube with inner diameter that incorporates consideration of the viscosity of the raw material liquids. In our experiment, the viscosity of the raw material slurry used in the LTA-type zeolite synthesis was 27.2 mPa·s (at 25 °C), which has a certain degree of viscosity. It is therefore suitable for synthesis with this semiflow MW reactor. From the viewpoint of the mass transfer, the raw material

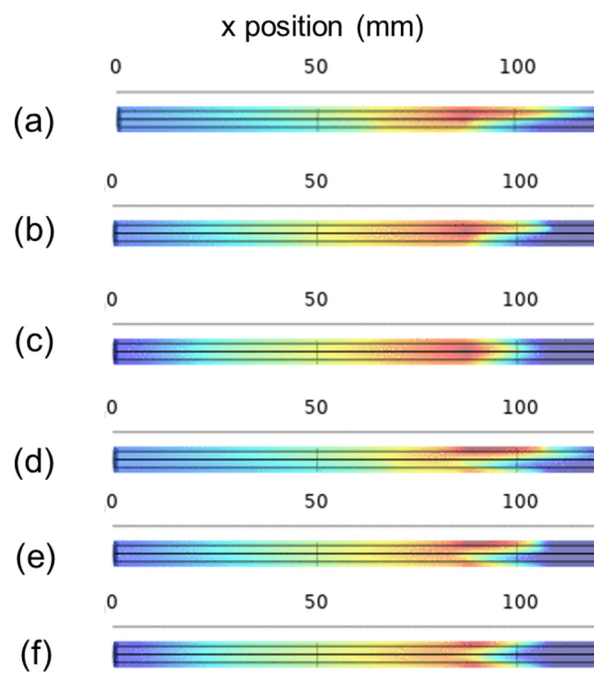


Figure 6. Effects of liquid viscosity (μ) on thermal distribution of semiflow reactor when the resonator moves from 0 to 90 mm: (a) MW heating, $\mu = 1$ mPa·s; (b) MW heating, $\mu = 10$ mPa·s; (c) MW heating, $\mu = 100$ mPa·s; (d) CH, $\mu = 1$ mPa·s; (e) CH, $\mu = 10$ mPa·s; and (f) CH, $\mu = 100$ mPa·s.

slurry was not mechanically stirred during MW heating. However, a single-phase material was obtained by X-ray diffraction of the LTA-type zeolite. Because numerical calculation results indicated local agitation from heat convection, the mass transfer which was presumed to be necessary for particle synthesis was conducted. When synthesizing materials using this semiflow system, it is noteworthy that raw materials with a higher viscosity showed better uniformity of heating, but more mass transfer is suppressed.

CONCLUSION

We developed a semiflow MW reactor able to perform material synthesis similarly to a flow MW reactor by moving the resonator instead of the raw material. This developed reactor is effective for processes that use slurry raw materials that are difficult to handle using conventional flow processes. Results indicate that the LTA-type zeolite has features similar to those of material synthesized using the flow reactor. Furthermore, the synthesis of nanosized FAU-type zeolite with a large specific surface area was achieved, which revealed that the semiflow MW reactor presents benefits for synthesizing nanocrystals from raw materials that entail difficulties, which hinder processing in a flow reactor. This developed reactor was also suitable for syntheses, including syntheses of large particles such as zeolite synthesis from coal fly ash. Numerical calculations show that homogeneous heating can be achieved using a reaction tube with an inner diameter that includes consideration of the raw material slurry viscosity. This process is a promising candidate not only for zeolite particle synthesis but also for various chemical processes, especially those for which slurry raw materials present barriers that hinder process construction.

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Author Contributions

The manuscript was composed through the contributions of all authors. All authors have approved the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

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