Morphology Control and Interlayer Pillaring of Swellable Na-taeniolite Mica Crystals

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Abstract

Na-taeniolite ($NaMg_2LiSi_4O_{10}F_2$) mica crystals were synthesized from nonstoichiometric raw batches containing NaCl as a flux, in order to control the morphology of mica crystals. Swellable Na-taeniolite was obtainable from both stoichiometric and nonstoichiometric batches although small amounts of different products were coprecipitated, depending on the composition of the raw batches. Samples obtained from raw batches containing ≤ 1 mol NaCl consisted of a single-phase swellable mica. The addition of a small amount of NaCl was effective in controlling the morphology of the mica crystals. Raw batches containing 1 mol NaCl yielded mica crystals having a hexagonal, plate-like morphology with a larger aspect ratio. Alumina-pillared micas prepared from host micas thus obtained from raw batches containing NaCl had larger specific surface areas than those obtained from stoichiometric batches. This suggests that the swellability of mica crystals is also affected by the addition of NaCl.

Keywords: Swellable fluorine mica, Flux, Intercalation, Alumina-pillared fluorine mica

1. Introduction

Micas constitute a major group in clay minerals. Naturally occurring micas do not exhibit swellability in water. However, some synthetic fluorine micas can swell with water. Na-taeniolite, which has the anhydrous structural formula $NaMg_2LiSi_4O_{10}F_2$, is a typical species of synthetic swellable fluorine mica [1-3]. Synthetic swellable micas are characterized by a large cation exchange capacity, high crystallinity and high thermal durability. Na-type swellable brittle micas (Na-n-mica, n = 2, 3 and 4) [4-8] are other interesting species of synthetic fluorine mica. Park et al. reported the phase pure Na-4-mica synthesized by NaCl melt method to avoid the excess use of NaF and pointed out that the crystal size of mica could be manipulated by the molar ratio of NaCl [4]. Ravella and Komarneni synthesized swelling micas using stoichiometric amount of fluoride by NaCl melt method [5]. Swelling micas were obtained by simple washing of the as-prepared products with deionized water [4,5].

Clay-based intercalation compounds and hybrid materials attract much attention because of their interesting properties, for example, adsorption and catalysis, as well as environmental preservation and remediation [9,10]. The host clays most extensively studied are smectite group minerals, such as a naturally occurring montmorillonite. Synthetic swellable fluorine micas can also be used as host crystals for intercalation [11-13]. Through synthesis, the morphology of clay mineral crystals becomes controllable [14]. The morphology control of Na-taeniolite crystals is significant for their use as host crystals to yield high performance intercalation compounds and for finding new application.

Intercalation of bulky inorganic polycations into the interlayer region of swellable micas by cation exchange and subsequent heating treatment produces thermally stable microporous solids, i.e., pillared micas [15-20]. These pillared micas retain features of the host micas, such as a large crystal size. In the present study, Na-taeniolite mica crystals were synthesized from stoichiometric and nonstoichiometric raw batches containing NaCl as a flux, in order to control the morphology of mica crystals for the purpose of yielding more promising host crystals. The micas obtained were also used to synthesize pillared micas with microporosity in their interlayer region.

2. Experimental

Reagent-grade SiO_2 (99.9%, Wako Pure Chemical Industries, Osaka, Japan), MgO (99.9%, Wako Pure Chemical Industries), LiF (99.9%, Wako Pure Chemical Industries)and NaF(99%, Wako Pure Chemical Industries) were used as raw materials and mixed in the proportions corresponding to Na- taeniolite to obtain a stoichiometric raw mixture. Reagent-grade NaCl (99.5%, Wako Pure Chemical Industries) was added to the stoichiometric mixture to obtain nonstoichiometric raw batches. The amount of NaCl was varied from 0.1 to 9 mol against 1 mol of Na-taeniolite. The use of NaF as a flux, instead of NaCl, was also examined.

Each batch was sealed in a platinum tube and heated at 950°C or 1100°C for 2 h using an electric furnace (FUH712, Advantec, Tokyo, Japan). The temperature was then lowered at a rate of -10°C/min to 950°C and the tube was removed from the furnace to cool in air. The as-prepared mica samples thus obtained were crushed and then washed with distilled water to rinse out the residual NaCl. The mica samples, hereafter abbreviated as xNaCl-y where x and y indicate the amount of NaCl (mol per 1 mol of Na-taeniolite) and the heat-treatment temperature, respectively, were characterized by XRD (XRD-6000, Shimadzu, Kyoto, Japan, using monochromatic CuKα radiation), FT-IR (FT/IR-4200, JASCO, Tokyo, Japan, using KBr tablet method) and SEM (S-4100, Hitachi, Tokyo, Japan).

Some of the samples (0NaCl and 1NaCl-series micas) were then transformed into Li^+-exchanged forms by repeated treatment with a 2 mol/L LiCl aqueous solution [16]. The Li^+-exchanged micas were reacted with a polyhydroxoaluminum (PHA) solution [17,21], which had an OH/Al ratio of 2.50 and an Al concentration of 0.05 mol/L, at 60°C for 2 h under vigorous stirring. The products were washed 10 times, dried at 60°C and then calcined at 400-700°C for 2 h to obtain microporous alumina-pillared micas. The pillared micas were characterized by XRD and N_2 adsorption-desorption at liquid nitrogen temperature (ASAP-2010, Micromeritics, USA). The BET specific surface area and pore size distribution (BJH) of the pillared micas were evaluated from N_2 adsorption isotherms.

3. Results and discussion

Figure 1 shows XRD patterns of the products obtained from different raw batches at 1100°C. Swellable Na-taeniolite could be obtained from both stoichiometric (0NaCl) and nonstoichiometric (1-9NaCl) batches; the sharp (001) diffraction peak at 7.2° (CuKα) and high order (00*l*) peaks were assignable to a single-layer hydrate state of the swellable mica [1]. The residual NaCl in the as-prepared products could be rinsed out thoroughly by simple washing with distilled water. Thus, this washing process resulted in a marked increase in the 001 peak intensity owing to the dissolution of the NaCl phase.

Unknown phases coprecipitated in the samples obtained from Na-rich raw batches ($\geq$ 3 mol NaCl). These impurity phases could not be removed from swellable mica even after multiple rinses with distilled water. By contrast, XRD patterns of the products obtained from raw batches containing 0 or 1 mol NaCl indicated that only mica was formed, suggesting that Na-taeniolite and NaCl are immiscible for a NaCl content of $\leq$ 1 mol.

Figure 2 shows XRD patterns of the products obtained from raw batches containing $\leq$ 1 mol NaCl at 1100°C and 950°C. Swellable Na-taeniolite was formed as a single phase at 1100°C although a small amount of SiO_2 coprecipitated in the 0NaCl-950 and 0.1NaCl-950 samples.

Heat-treatment temperatures between 950 and 1100°C did not yield homogeneous melting, but they gave sintered products. Swellable Na-taeniolite series fluorine micas were synthesized as a single phase from the stoichiometric raw batch by melting in a sealed platinum tube at 1400-1420°C [1,2]. A preliminary study also showed that synthesis by the melting method at 1250°C or 1400°C yields swellable micas. However, it is found that the morphology of the mica crystals obtained at these higher temperatures is hardly controllable.

Figure 3 shows SEM micrographs of Na-taeniolite obtained at 1100°C and 950°C from different raw batches. All the samples show typical flake-like crystals of synthetic micas. Clearly, the addition of a small amount (0.1-1 mol) of NaCl is very effective in controlling the morphology of Na-taeniolite crystals. Raw batches with even a very low NaCl content (0.1 mol) yielded mica crystals having a more defined shape compared to those obtained from the stoichiometric raw batch. In addition, the raw batch containing 1 mol NaCl yielded mica crystals having a hexagonal, plate-like morphology (maximum dimension of >10 μm) with a larger aspect ratio.

In the experiments using nonstoichiometric raw batches containing excess NaF instead of NaCl, the SiO_2 and/or $NaMgF_3$, which could not be rinsed out with water, inevitably coprecipitated. The morphology of mica crystals was virtually unaffected by NaF content. Park et al. reported the synthesis of Na-4-mica using near-stoichiometric powder mixtures containing NaCl [4]. Although the starting materials, synthetic conditions and species of mica are different, the NaCl in the raw batches plays important roles in the formation of mica crystals in the present study. In addition, the use of a stoichiometric amount of NaF prevents the undesirable release of fluorides into the environment during the synthesis of fluorine micas [5] if an unsealed crucible is used in the heating process of raw batches. These facts show that the use of nonstoichiometric raw batches containing NaCl is a very effective option for the synthesis of swellable Na-taeniolite having controlled morphology, without the coprecipitation of insoluble impurities.

Figure 4 shows IR spectra of Na-taeniolite obtained from raw batches containing ≤1 mol NaCl at 1100°C. The absorption bands at around 980 and 1110 cm^{-1} are assignable to e^1_1 and a^1_1 mode, respectively, based on a $(Si_2O_5)_n$ normal vibration model [1,2]. These two bands showed no change regardless of NaCl content in the range from 0NaCl to 1NaCl. The bands at around 710 and 470 cm^{-1}, which are assignable to a^2_1 and e^2_1 mode, respectively, also showed no change. Kitajima et al. pointed out that the tetrahedral lattice vibrations are affected by the magnitude of the layer charge and/or the changes in octahedral and interlayer compositions [1,3]. Consequently, judging from the IR spectra, these micas have the same chemical composition despite their different morphologies. Even at low contents, the NaCl in the raw batches acts as a flux, affecting the diffusivity of the constituent ions of the mica. Thus, the size and shape of the mica crystals changed depending on the NaCl content.

Figure 5 shows XRD patterns and changes in BET specific surface area of alumina-pillared micas obtained from 0NaCl-1100 and 1NaCl-1100 micas as host crystals. The PHA solution used as a pillaring agent contains bulky Keggin Al_{13} polycations [17, 21]. The pillared mica obtained from 0NaCl-1100 gave a (001) reflection having a long basal spacing of 1.8 nm at around 4.8° (CuKα) along with a strong peak having a small basal spacing at around 7°, indicating coexistence of two different interstratified structures with different basal spacings. The former phase has an interlayer distance of about 0.9 nm, which is calculated by subtracting the thickness of the silicate layer from the basal spacing. The latter phase, which is probably identified as unreacted mica, deteriorates the microporosity of the product because of its narrow interlayer regions. The (001) reflection around 4.8° (CuKα) increased in intensity for the pillared mica obtained from 1NaCl-1100, while the intensity of the peak around 7° decreased markedly. This suggests that the swellability of mica crystals is also affected by the addition of NaCl. Although the exact reasons remain unclear, NaCl as a flux may help to prevent the fixation of interlayer Na^+ ions into the hexagonal holes of the silicate layers during the formation of mica crystals so that the addition of NaCl enhances the swellability of mica crystals.

In our previous study on complex formation through intercalation using Na-taeniolite series swellable fluorine micas [$Na_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2$] [16], pillared micas having ideal stacking sequences were formed only when host crystals were transformed into Li^+-exchanged forms before the intercalation of pillaring species. The Li^+-exchanged forms have an improved swellability to allow intercalation of bulky cations. In the present study, the transformation into Li^+-exchanged forms was also necessary to yield the pillared phase having a 1.8 nm basal spacing.

The pillared micas prepared from 1NaCl-1100 had larger specific surface areas than those obtained from 0NaCl-1100 (Fig. 5 (b)). Pore size distribution curves shown in Fig.6 supported the higher microporosity of the pillared micas prepared from 1NaCl-1100. However, the specific surface areas of the pillared micas prepared from 1NaCl-950 were smaller than those from 1NaCl-1100; for example, the pillared mica obtained from 1NaCl-950 at the calcination temperature of 400°C gave a BET specific surface area of 100 m^2/g. These results show that the products obtained from 0NaCl-series host micas contain a 1.2-nm phase, which cannot contribute to microporosity, and the swellability of mica crystals is also affected by the synthesis temperature.

Intercalation compounds, including interlayer pillared porous materials, are generally produced using naturally occurring swellable clay minerals, typically montmorillonite. However, the present study shows that synthetic swellable fluorine micas with controlled morphology, characterized by larger and more clear-cut flakes, may impart unique characteristics to intercalated materials.

4. Conclusions

The addition of NaCl (0.1 to 1 mol against 1 mol of Na-taeniolite) to raw batches proved very effective in controlling the morphology of Na-taeniolite crystals. NaCl added to the stoichiometric raw mixture probably acts as a flux, improving the diffusivity of the constituent ions of the mica during the formation process. The mica crystals thus obtained from the raw batches containing NaCl were larger and had more defined shapes and higher aspect ratios compared to those obtained from the stoichiometric raw batch. The addition of NaCl also improves the swellability of Na-taeniolite crystals, leading to the formation of interlayered compounds with higher microporosity.

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Figure captions

Fig. 1 XRD patterns of products obtained from stoichiometric and nonstoichiometric batches at 1100°C.

Fig. 2 XRD patterns of products obtained from different raw batches containing 0-1 mol NaCl at (a) 1100°C and (b) 950°C.

Fig. 3 SEM micrographs of Na-taeniolite crystals. (a) 0NaCl-1100, (b) 0.1-NaCl-1100, (c) 1NaCl-1100, (d) 0NaCl-950, (e) 0.1NaCl-950 and (f) 1NaCl-950.

Fig. 4 IR spectra of Na-taeniolite samples obtained from different raw batches containing 0-1 mol NaCl at 1100°C.

Fig. 5 (a) XRD patterns of alumina-pillared micas obtained from 0NaCl-1100 and 1NaCl-1100 at a calcination temperature of 400°C and (b) BET specific surface area of the alumina-pillared micas plotted against the calcination temperature.
●: pillared mica obtained from 1NaCl-1100 and ■: pillared mica obtained from 0NaCl-1100.

Fig. 6 Pore size distribution curves of alumina-pillared micas obtained from 0NaCl-1100 and 1NaCl-1100 at a calcination temperature of 400°C

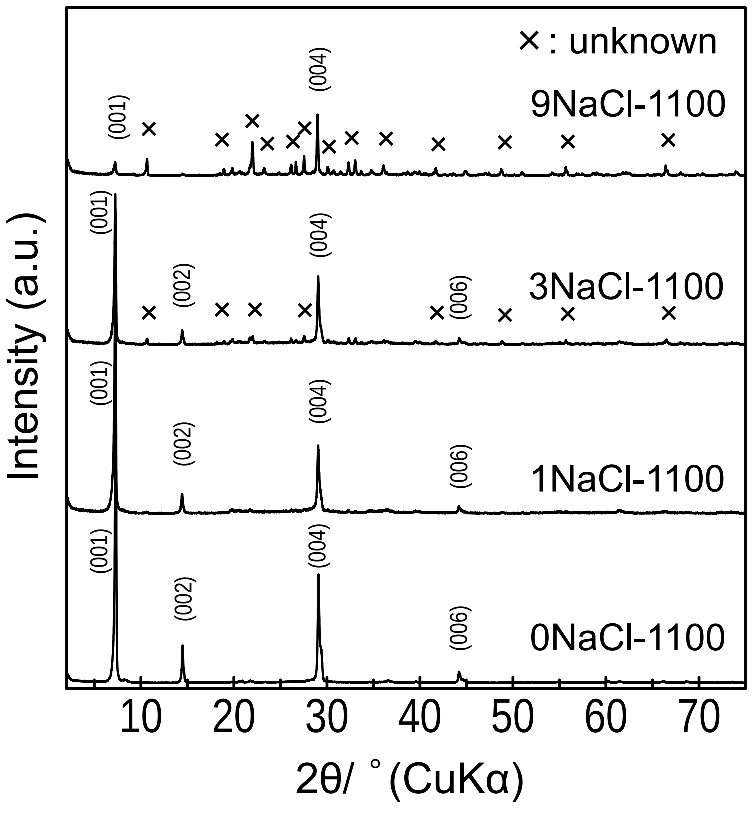
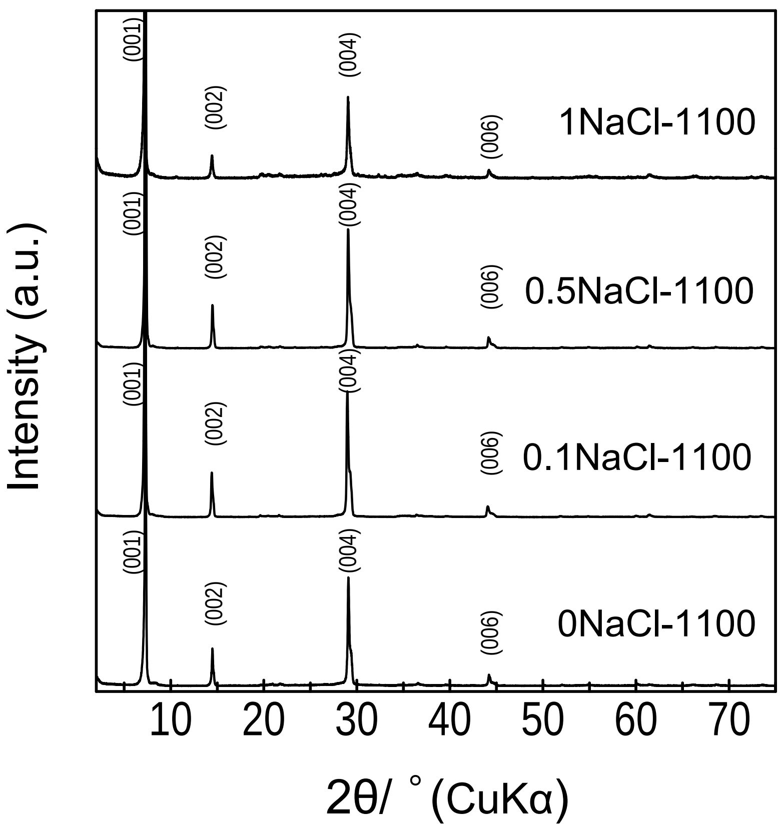

× : unknown
9NaCl-1100
3NaCl-1100
1NaCl-1100
0NaCl-1100
(001)
(002)
(004)
(006)
Intensity (a.u.)
10
20
30
40
50
60
70
2θ/ °(CuKα)

Fig. 1

(a)



Intensity (a.u.)
(001)
(002)
(004)
(006)
1NaCl-1100
0.5NaCl-1100
0.1NaCl-1100
0NaCl-1100
10
20
30
40
50
60
70
2θ/ ° (CuKα)

Fig. 2(a)

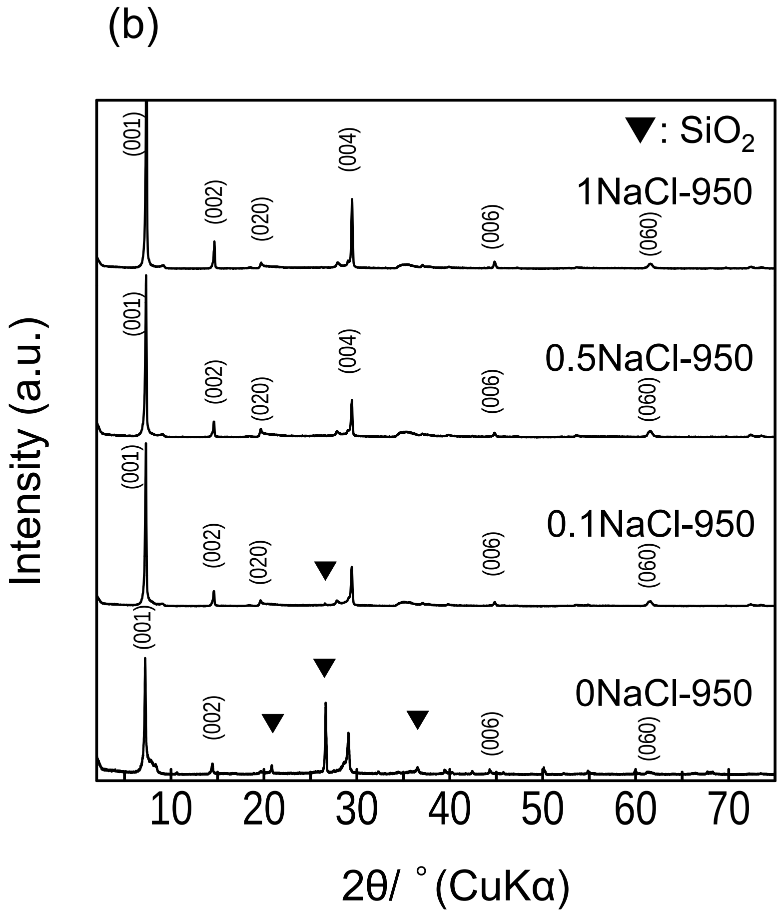

(b)
▼: SiO_2
1NaCl-950
0.5NaCl-950
0.1NaCl-950
0NaCl-950
(001)
(002)
(020)
(004)
(006)
(060)
Intensity (a.u.)
10
20
30
40
50
60
70
2θ/ ° (CuKα)

Fig. 2(b)

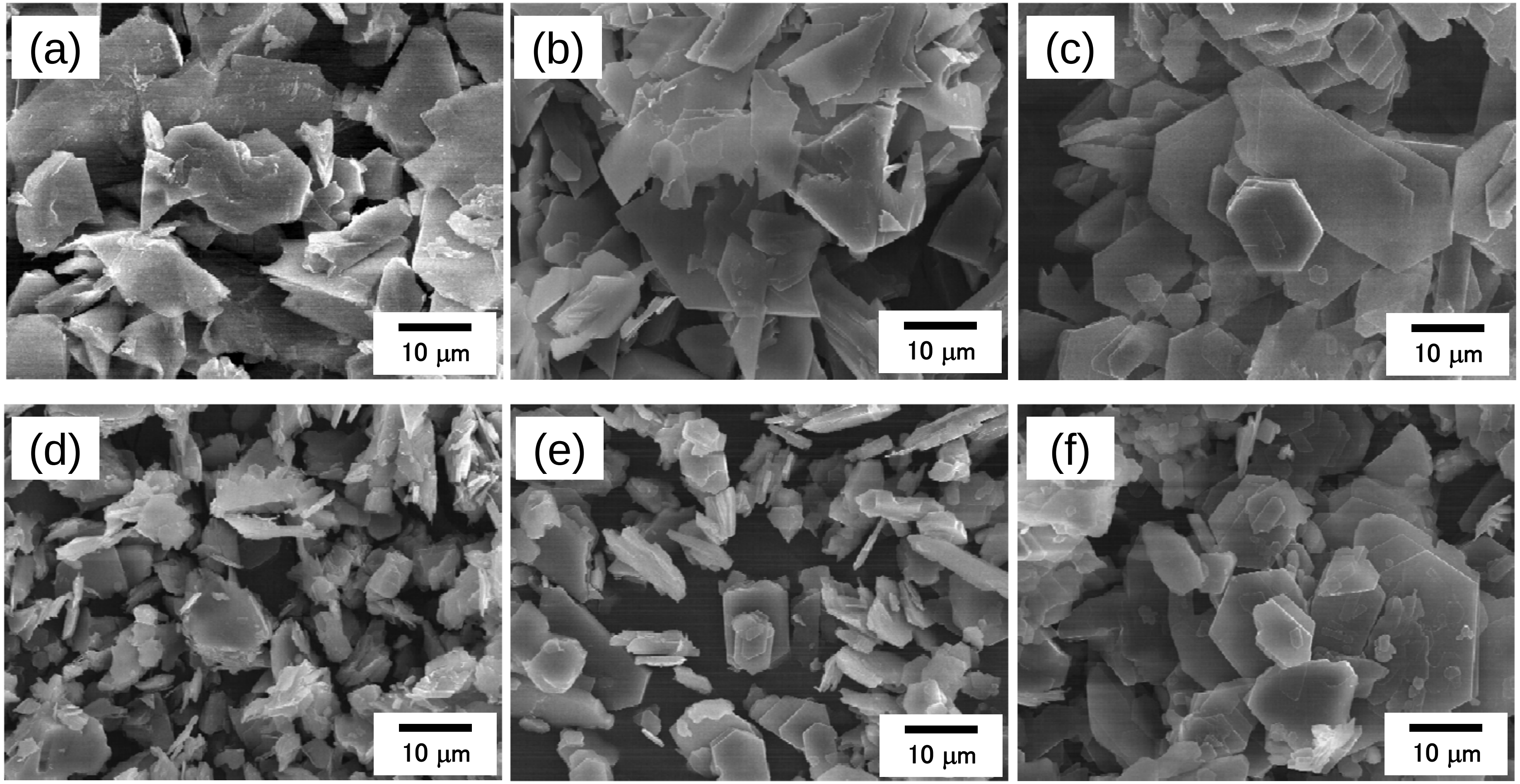


Fig. 3

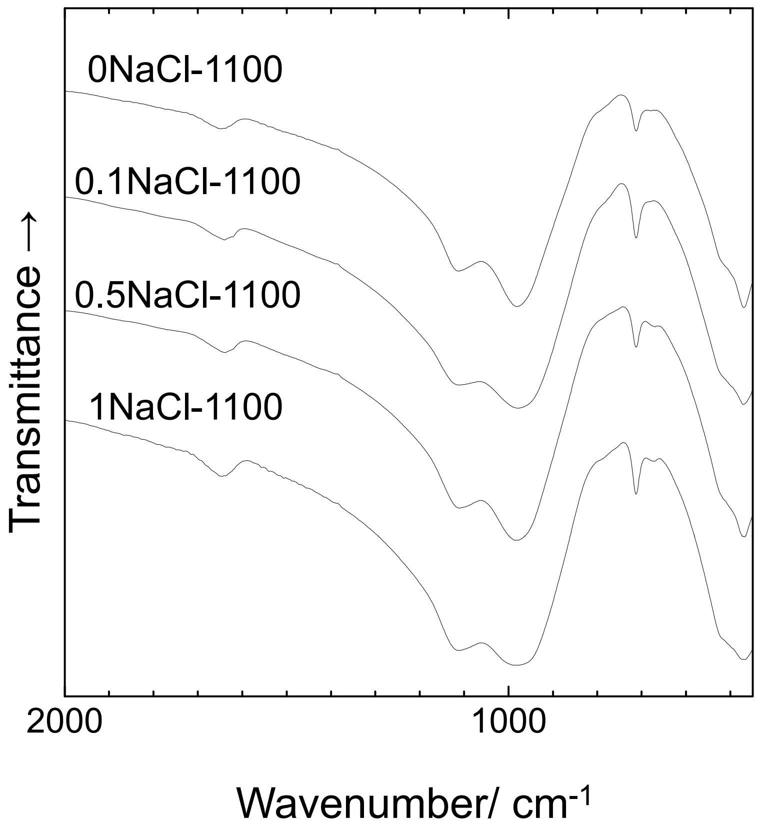

0NaCl-1100
0.1NaCl-1100
0.5NaCl-1100
1NaCl-1100
Transmittance →
2000
1000
Wavenumber/ cm^{-1}

Fig. 4

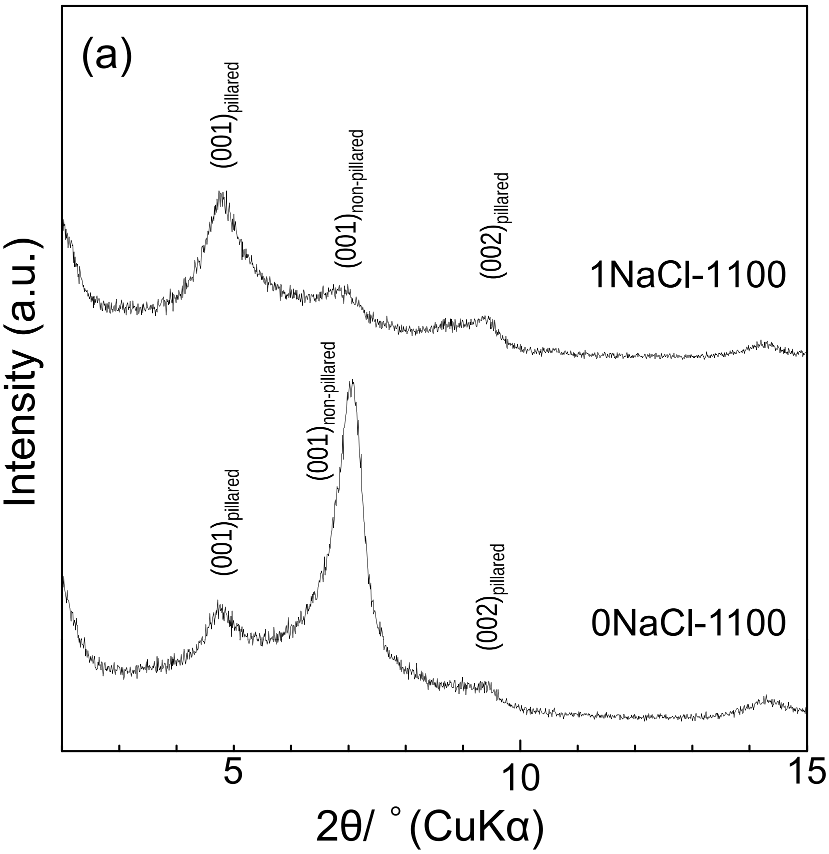

(a)
(001)pillared
(001)non-pillared
(002)pillared
1NaCl-1100
(001)pillared
(001)non-pillared
(002)pillared
0NaCl-1100
Intensity (a.u.)
5
10
15
2θ/ °(CuKα)

Fig. 5(a)

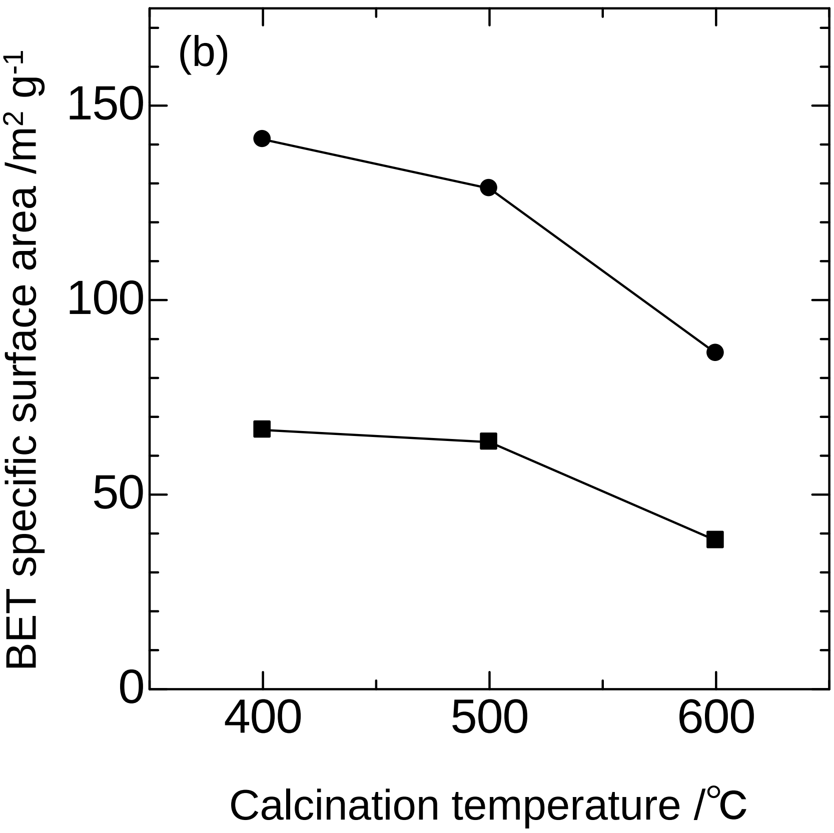
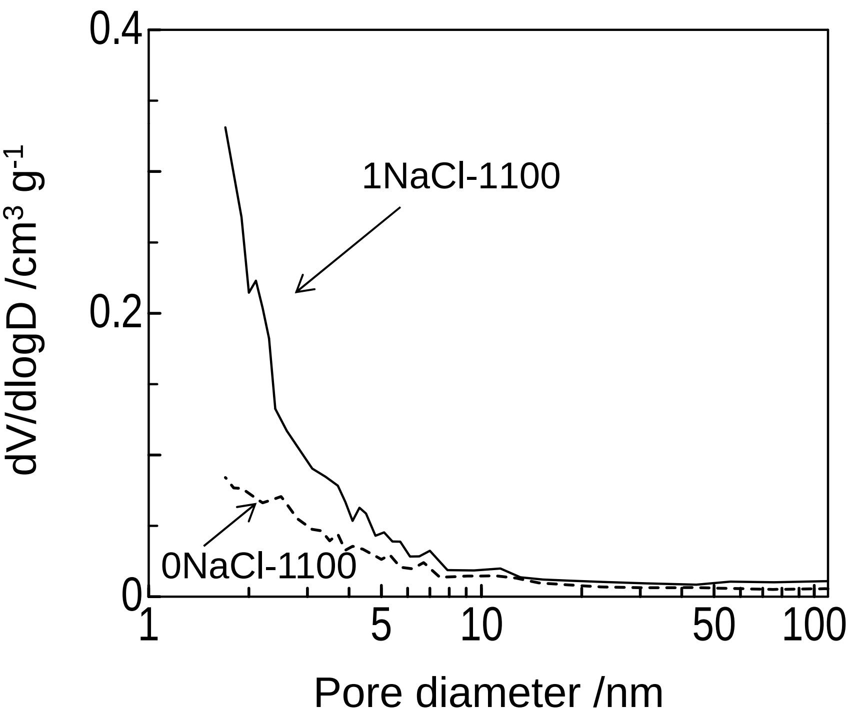

(b)
BET specific surface area /m^2 g^{-1}
0
50
100
150
400
500
600
Calcination temperature /℃

Fig. 5(b)



0.4
0.2
0
dV/dlogD /cm^3 g^{-1}
1NaCl-1100
0NaCl-1100
1
5
10
50
100
Pore diameter /nm

Fig. 6