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Preparation of zeolite sheet using a papermaking technique

Part II *The strength of zeolite sheet and its hygroscopic characteristics*

H. ICHIURA,* N. OKAMURA, T. KITAOKA, H. TANAKA
Department of Forest Products, Kyushu University, Fukuoka 812-8581, Japan

Zeolite has been widely applied to practical processes in various industrial fields as a desiccant, an adsorbent, a molecular sieve, an ion exchanger, a catalyst and so on. It has generally been used in the form of beads or pellets. However, these methods of utilization have some disadvantages such as powdering of the zeolite when particles rub against each other and remarkable pressure losses in reaction towers with increasing gas flow velocities. Zeolite sheets consisting of 10% cotton linters pulp, about 30% ceramic fiber and 60% zeolite were easily prepared using a papermaking technique intending to produce their honeycomb structure. The sheets were ignited at 700°C to remove linters pulp, but they were fragile and brittle. To improve the zeolite sheet strength, alumina sol was used as a binder. Although a very high retention of alumina was achieved by the internal addition method with polymer retention aids, the improvement of sheet strength was not satisfactory. In this case, the added alumina seemed to be located mainly on the outermost surface of the sheet because the retention of alumina occurred through the filtration. On the other hand, soaking of zeolite sheets in the alumina sol increased the sheet strength remarkably. These results suggested that the alumina was distributed in the whole sheet and formed a tight network structure between particles. These procedures are expected to lead to useful zeolite products, which have a potential for new practical uses.

1. Introduction

Recently, nitrogen oxides (NO_X) and sulfur oxides (SO_X), and carbon dioxide (CO_2) have been identified as causes of acid rain and global warming, respectively. Factories, power plants and automobiles discharge large quantities of these environmental pollutants. Zeolite has been used as a material which removes NO_X, SO_X and CO_2. Studies on zeolite in these fields have been actively undertaken [1–3] and a number of artificial zeolites are now commercially available.

Zeolite, which is a hydrated alkali-aluminium silicate, has a characteristic three-dimensional structure [4, 5], and zeolites have been used in various applications such as desiccants, adsorbents, molecular sieves, ion exchangers and catalysts [6–12]. In general, zeolites have usually been used as beads or pellets [13]. However, they have serious disadvantages, such as a pressure loss in the reaction tower, powdering of the zeolite when the particles rub against each other, and difficulties in repacking them. It has been desired, therefore, to overcome these drawbacks. The honeycomb structure has a bright prospect of removing these defects in beads and pellets [14–16]. An extrusion method has mainly been applied to make the honeycomb [13], but this is not a useful procedure for zeolite because its characteristic porous structure is easily destroyed by the high extrusion pressure. Papermaking techniques have therefore been tried [17–20] to prepare the zeolite sheet instead of the extrusion method. The techniques give a material with the following characteristics: light weight, large surface area, high homogeneity, easy handling and flexibility of processing.

In the previous study [20], it was reported that the retention of inorganic compounds exceeded 90% when a dual polymer system using both cationic and anionic polymers was employed. The sheets were however fragile and brittle after they had been ignited up at 700°C to remove wood pulps. Accordingly, an improvement in the sheet strength was a mandatory requirement before the technique could be used for any practical application.

In this work, various binder treatments were attempted to improve the strength of the zeolite sheets. An alumina sol was the most useful to achieve the required practical strength level. One of the improved

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[*] Research Fellow of the Japan Society for the Promotion of Science.

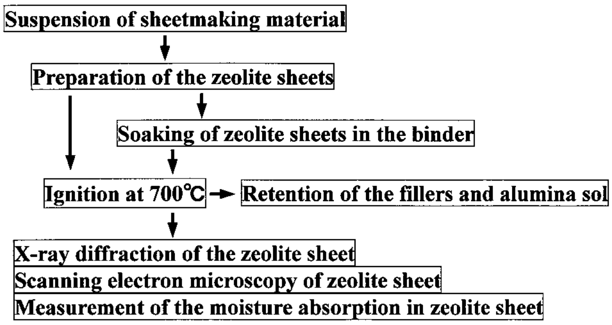


Figure 1 The sequence of the experiments.

characteristics of the zeolite sheet was confirmed by the extremely high rate of moisture adsorption.

2. Experimental

The sequence of experiments is shown in Fig. 1.

2.1. Materials

The pulp used was a cotton linters pulp, which was beaten to a Canadian Standard Freeness (CSF) of 333 ml in a Tappi (Technical Association of Pulp and Paper Industry) standard beater.

Inorganic materials (fillers) used were zeolite Y type, and ceramic fibers kindly provided by Mitsubishi Heavy Industry.

Poly (diallyldimethylammonium chloride) (PDADMAC) and anionic polyacrylamide (A-PAM) were used as retention aids in the same way as in the previous report [20].

In the case of internal addition of alumina sol as a binder, the cationic and anionic flocculants were Akyurakku 135 and Akyurakku 304E (Mitsui Cytec Ltd.), respectively. The alumina sol (Alumina sol 520) was kindly donated by Nissan Chemical Co.

2.2. Preparation of the zeolite sheet

The pulp slurry was mixed with cationic flocculant, followed by the addition of inorganic suspension including zeolite and ceramic fiber, 0% or 60% alumina sol on zeolite and anionic flocculant in that order. Handsheets with a grammage of 200, 250 or 300 g/m^2 were prepared according to Tappi method - 205. The wet sheets were pressed under 350 kPa for 5 minutes and dried in a convection oven at 105°C for 30 minutes.

2.3. Drainage time

The time required for water drainage from a stock suspension through a wire mesh screen of a standard laboratory sheetmaking machine was determined visually using a stopwatch.

2.4. Impregnation of zeolite sheets with binder

After soaking zeolite sheets in binders ranging in concentration from 5% to 20%, the sheets were pressed under 350 kPa for 5 minutes and were then kept in an air-conditioned chamber (20°C, 65% RH) for 24 hours.

2.5. Retention of inorganic materials

The retention of inorganic materials was estimated from the ash contents of the sheets determined by igniting the sheets in an electric furnace at 700°C for 20 minutes. These values were corrected for the weight losses of the inorganic materials themselves determined by ignition of blank samples in a similar manner.

2.6. X-ray diffraction measurement of the alumina and zeolite sheets

The crystal structures of alumina and zeolite in the sheets were determined using an X-ray diffractometer (XD-D1, Shimazu). X-ray generation conditions were 30 kV and 40 mA. The scanning rate and range were 2°/min and 5–90° (2θ), respectively. The analyses were performed on at least three different locations of each sheet.

2.7. Retention of alumina sol

The zeolite sheets with alumina were powdered for the X-ray diffraction studies. The retention of the alumina was quantified using the relationship (calibration curve) between the weight ratio of mixed powder (alumina/zeolite) and the peak intensity ratios of the zeolite ($2\theta = 6.20°$) and alumina ($2\theta = 67.0°$) prepared previously [21].

X-ray diffraction patterns were recorded on a Shimadzu XD-D1 X-ray diffractometer fitted with a vertical goniometer using Cu K_α irradiation ($\lambda = 1.5418$). The scanning speed was 1°/min for angular ranges of 5–10°(2θ) and 60–70°(2θ). X-ray generation conditions were 30 kV and 40 mA.

2.8. Scanning electron microscope (SEM) studies of zeolite sheets

The surfaces of the zeolite sheets were observed by SEM (JSM-5600, JEOL) after carbon coating of the zeolite sheet. The electron accelerating voltage was 10 kV and the magnification was 400×.

2.9. Strength of zeolite sheets and adsorption of moisture by the sheets

After conditioning the sample sheets at 20°C and 65% RH for more than 24 hours, their strengths were evaluated as the maximum compressive load, according to the ring crush test, Tappi method - 818.

The moisture adsorptivity was evaluated for the zeolite sheets containing binder. The dried sheets were quickly transferred to a desiccator having an atmosphere saturated with deionized water at 20°C. The weight of this sheet was measured at suitable time intervals. The percentage moisture gain was given by:

$$W(\%) = (W_t - W_0)/W_0 \times 100$$

where W_t = the weight of the zeolite sheet after moisture adsorption, W_0 = the dry weight of the zeolite sheet.

3. Results and discussion

3.1. Retention of alumina sol in the sheet web by internal addition

The effect of the flocculants on the retention of the inorganic materials containing zeolite, ceramic fiber and alumina sol was examined in connection with the internal addition of the alumina sol.

When PDADMAC and A-PAM were used as in the previous report [20], the retention of inorganic materials was less than 30% whereas, in the retention system using cationic and anionic flocculants, Akyurakku 135 and 304E, the retention of inorganics increased to about 70%. The latter system was therefore adopted as the flocculants for the internal addition method.

The retention of alumina increased with increasing dosage of flocculants and at the same time the drainage time became significantly longer. The relationship between drainage time and retention of alumina is shown in Fig. 2. It was estimated that the retention of alumina sol was mainly achieved by a physical mode of action due to filtration rather than by a chemical fixing due to the flocculants. Because of the micro-particles of alumina, in other words because of the huge surface area of the alumina, the levels of addition of the flocculants, 1.0%–2.0% on total solids was inadequate. This situation is shown by the very low retention of inorganics like zeolite, while the retention of inorganics in the absence of alumina was about 90%, as described in the previous paper [20]. The retention of inorganics including alumina was somewhat improved by increasing the amount of added flocculants. The strength of sheets was not however satisfactory, even at the high content of alumina achieved by the higher level of addition of flocculants. It was, therefore, assumed that this procedure would be rather impractical in mills because of its high cost.

3.2. The strength of zeolite sheets after soaking treatment in a binder solution

The retention of alumina sol by the soaking method was almost 100% because of physical entrapment.

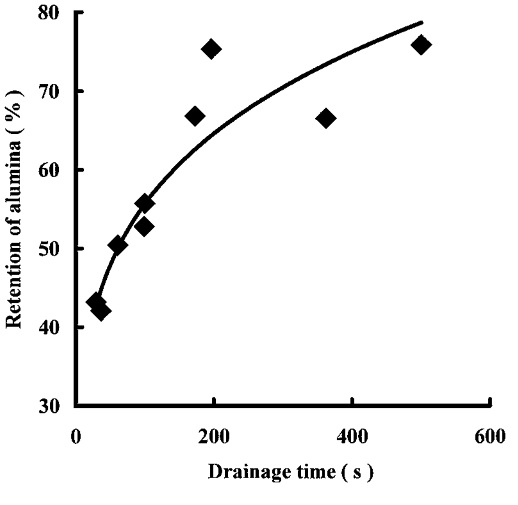


Figure 2 The relationship between the drainage time and the retention of alumina sol; Pulp 10%, zeolite 65.5%, ceramic fiber 24.5%; Alumina sol 60% on zeolite.

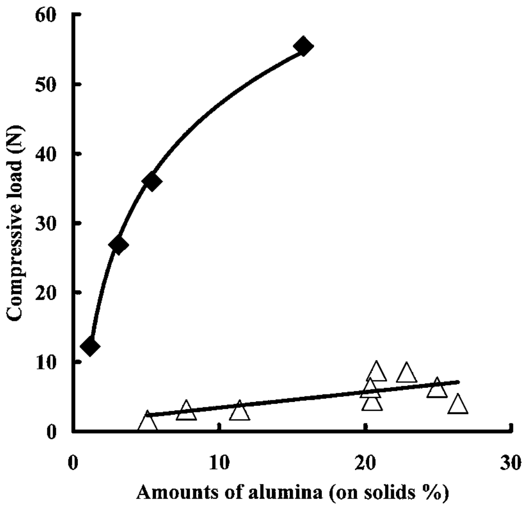


Figure 3 The effects of the amounts of alumina on the sheet strength, Pulp 10%, zeolite 65.5%, ceramic fiber 24.5%; The basis weight, 250 g/m^2; (◆) soaking; (△) internal addition.

Fig. 3 shows the sheet strength as a function of the amount of alumina in the sheets achieved by the soaking method and by internal addition of alumina sol.

The sheet strength was much greater for any given amount of alumina binder when the soaking method was used. It was thought that the sheet strength was improved because the binders were uniformly distributed in the sheet and that strong bonds were efficiently formed by a melting of the alumina particles on ignition at 700°C when the sheets were soaked in the alumina sol.

It was thought that the internal addition method was inferior because it was considered that the alumina sol added was then located mainly on the outermost surfaces of sheets, because the retention of alumina sol occurred through filtration, as mentioned previously.

Fig. 4 shows the effect of the inorganic fibers on sheet strength with soaking treatment in alumina sol.

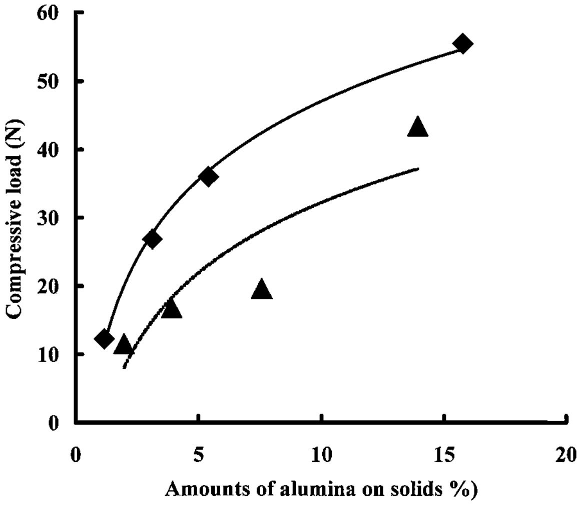
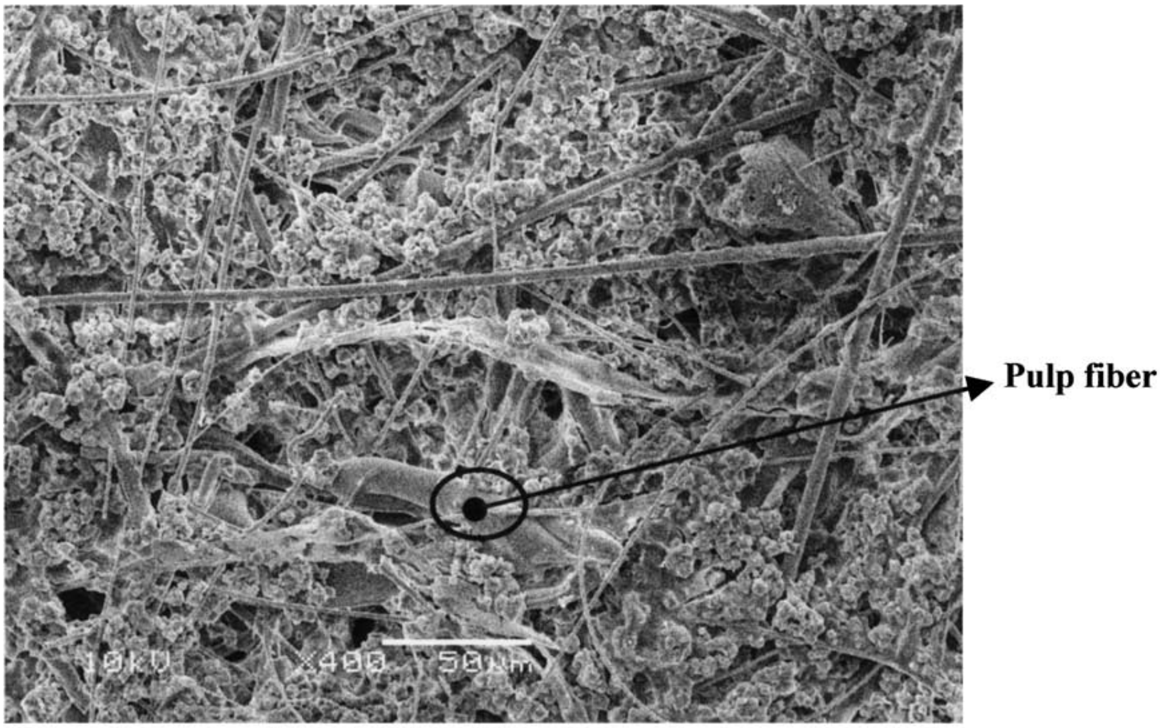


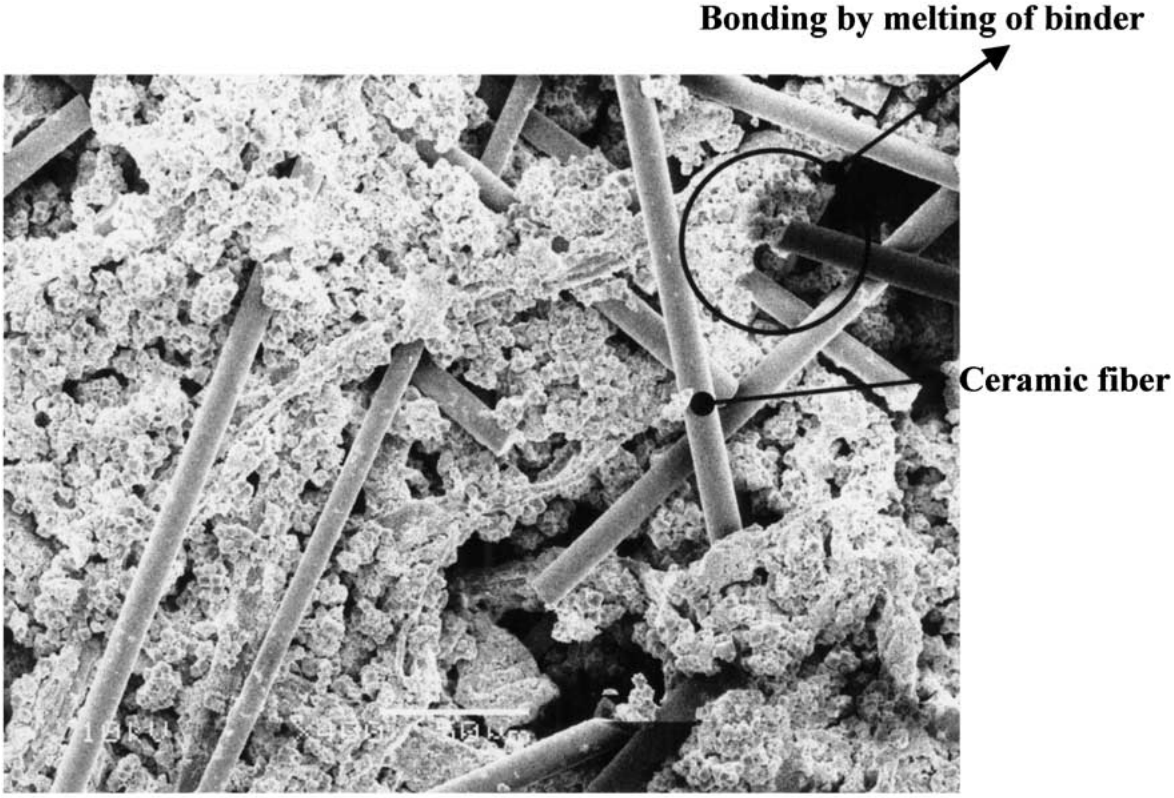
Figure 4 The effects of the inorganic fiber on the sheet strength, Pulp 10%, zeolite 65.5-80%, ceramic fiber 24.5 or 10%; the basis weight, 250 g/m^2; (◆) ceramic fiber 24.5%; (▲) ceramic fiber 10%

The preliminary study showed that the zeolite sheet without any inorganic fibers could not remain in the form of a sheet after ignition at 700°C. The sheet with 24.5% ceramic fiber was stronger than that with 10% ceramic fiber. These results indicated that the inorganic fiber was important for forming effective bonds due to the melting of the binder, and the content of the fiber could be chosen accordingly.

Fig. 5 shows SEM micrographs of the zeolite sheets before and after ignition. After ignition at 700°C, strong bonds between ceramic fiber and binder formed by the melting of alumina particles at 700°C were observed.



Before ignition at 700˚C



After ignition at 700˚C

Figure 5 SEM images of zeolite sheets before and after ignition at 700°C.

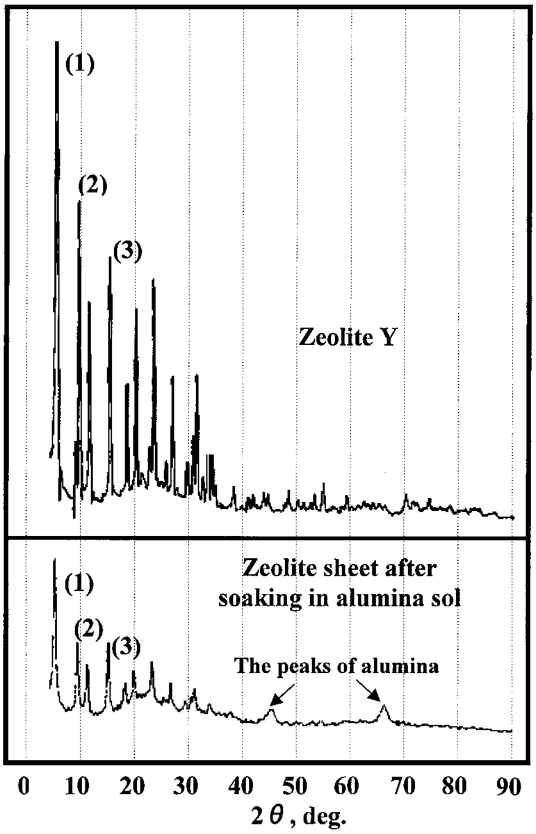


Figure 6 The diffraction pattern of the zeolite in the zeolite Y sheet with soaking treatment in alumina sol.

3.3. The function of zeolite sheets

The adsorptivity of a zeolite depends on the pore sizes and shapes that are characteristic of the zeolite. The zeolites have therefore been widely used as molecular sieves.

To determine whether or not the characteristics of the zeolite sheets were affected by the binder, the X-ray diffraction and the adsorption of moisture were studied.

Fig. 6 shows the diffraction patterns of zeolite Y and of the zeolite sheet after soaking in alumina sol. The diffraction pattern of the zeolite sheet after soaking in alumina sol and ignition at 700°C was similar to that of the zeolite Y type without heat treatment. The diffraction angle (2θ, deg)–and spacing (d, Å) for the three strongest peaks of the zeolite Y type were 6.24 deg–14.15 (1), 10.24 deg–8.63 (2), and 15.85 deg–5.59 (3). On the other hand, the values of 2θ–d for the zeolite sheet after soaking in alumina sol were 6.20 deg–14.25 (1), 10.11 deg–8.74 (2) and 15.72 deg–5.63 (3) which were very similar to those of zeolite Y. The results demonstrated that the original structure of zeolite in the sheet was maintained during the soaking treatment in the alumina sol and calcination at 700°C.

Fig. 7 shows the hygroscopicity of the zeolite sheet in comparison with that of related materials such as the commercial spherical zeolite (F type, Wako Pure Chemical Industries, LTD) and paper. The hygroscopic nature of the zeolite sheet was obviously greater than that of the paper or of the spherical zeolite. It is particularly noteworthy that the initial rate of moisture adsorption by the zeolite sheets is much greater than that in zeolite powder, spherical zeolite or paper.

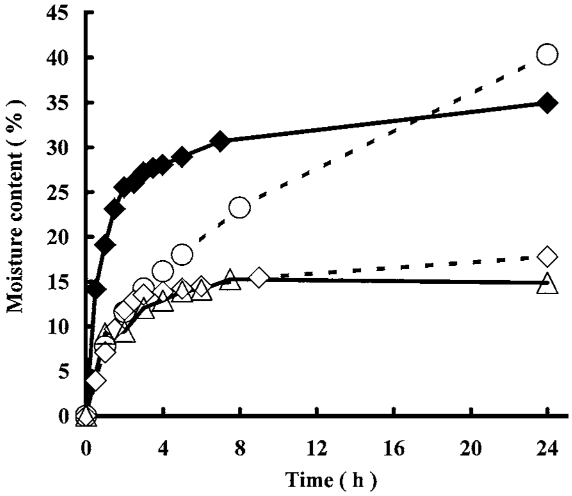


Figure 7 The hygroscopicity of the zeolite sheet, Pulp 10%, zeolite 65.5%, ceramic fiber 24.5%, (♦) zeolite sheet; (○) zeolite powder; (◇) spherical zeolite; (△) paper.

These results indicate that the zeolite sheets are excellent in quality and have a great potential for practical use.

4. Conclusions

In this study, the zeolite sheet was treated with a binder, alumina sol, in order to improve the sheet strength after ignition at 700°C. Internal addition did not give satisfactory sheet strength although the binder was retained in the zeolite sheet. However, soaking of the zeolite sheets in the binders was an extremely effective way of enhancing their strength after ignition at 700°C. Inorganic fiber such as ceramic fiber was indispensable to maintain the strength of the zeolite sheet after ignition at 700°C.

X-ray diffraction patterns revealed that the structure of the zeolite was virtually unchanged after the soaking treatment in the binder and ignition at 700°C. The hygroscopicity of the zeolite sheets was much higher than that of zeolite powder or commercial spherical zeolite.

The zeolite sheets are definitely expected to have a potential for practical use.

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