SYNTHESIS OF ALUMINA-PILLARED FLUORINE MICAS USING POLY(VINYL ALCOHOL) AS A TEMPLATE AND THEIR POROUS CHARACTERISTICS

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Synthesis of alumina pillared fluorine micas has been undertaken using synthetic high layer-charged expandable fluorine mica and hydroxoaluminum solutions with different solution loadings under the presence of poly(vinyl alcohol) (PVA) to obtain microporous solids having high thermal durability. The basal spacings and surface areas of the products depend on the solution loading. The optimal solution loading in this study was 24 mmol Al/g mica. The products thus obtained gave the large basal spacing of 2.7 nm at 500 °C and the maximum surface area of 403 m^2 g^{-1} at 600 °C. The surface area of the product was above 300 m^2 g^{-1} even after heating at 800 °C, showing high thermal durability. Pore size distribution of the products proved the existence of micropores. Sintered bodies of the alumina-pillared micas were obtained by firing at 500-700 °C using pressed powder compacts of the pillared micas. They were machinable and retained porous characteristics.

INTRODUCTION

Pillared clays exhibit interesting properties for catalysis, adsorption and separation. The intercalated oxides formed after calcination prop the layers apart as pillars in pillared clays.

The present authors have focused their attention on expandable synthetic fluorine micas [1, 2] as host crystals for intercalation. These synthetic micas are featured by large cation exchange capacity and high crystallinity. The variability of layer charge also leads to the controlled pillar density and microporous properties for alumina-pillared [3, 4], chromia-pillared [5], gallia-pillared [6] and titania-pillared [7, 8] fluorine micas. The machinable sintered bodies of alumina-pillared fluorine micas having micropores are also obtainable by firing powder compacts of the pillared micas at 500 - 700 °C without adding any binders [4].

Pillared clays have 2-dimensional pores in the interlayer region among pillars while zeolites have 3-dimensional pores in the crystal structure. In general, the pore size of pillared clays is larger than that of the zeolites and smaller than that of the inorganic mesoporous solids such as silica and alumina [9 - 12], and is controllable by choosing both host crystals and pillaring agents. The addition of polyvinyl alcohol (PVA) solution prior to intercalation is also effective to control porous properties of alumina-pillared clays [13].

In the present work, Na-tetrasilicic fluorine mica, [$NaMg_{2.5}Si_4O_{10}F_2$] [1, 4], has been used as the host crystals. The thermal durability and microporous characteristics for alumina-pillared micas prepared under the presence of PVA with different solution loadings in mmol Al in hydroxoaluminum solutions per 1 g of mica have been studied. The pillared micas have been characterized by X-ray diffraction and nitrogen adsorption-desorption analysis.

EXPERIMENTAL PART

The starting Na-tetrasilicic fluorine mica (hereafter denoted by Na-TSM), $NaMg_{2.5}Si_4O_{10}F_2$, was synthesized by the procedure described previously [1]. Hydroxoaluminum solution used as a pillaring agent was prepared by dissolving aluminum metal in HCl [14]. The solution had an OH/Al ratio of 2.50 and an Al_2O_3 concentration of 23.8 wt.%. The solution was diluted with distilled water before use. 14 g of the host mica crystals was dispersed into 500 cm^3 of distilled water to form a host suspension. Each host suspension was mixed with 250 cm^3 of PVA (the degree of polymerization: 1000) concentrated solution for 2 days and then allowed to react with the hydroxoaluminum solution under vigorous stirring at 65 °C for 3 days. The Al amount in the suspensions of host crystals were 6, 12, 24 and 44 mmol Al/g mica.

The reaction products were washed with distilled water repeatedly and then dried at 60 °C in air. The amounts of intercalated Al into host crystals were determined by a gravimetric analysis after the samples

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were fused with Na_2CO_3. The dried products were heated at the temperature range of 400 - 800 °C for 3 h. Basal spacings of the heated products, i.e. pillared micas, were determined by X-ray diffraction (XRD) using Cu*K*α radiation. Surface areas, pore volumes and pore size distributions of the heated products were evaluated from N_2 adsorption-desorption isotherms at liquid nitrogen temperature. The Barrett, Joyner and Halenda (BJH) method [15] was used to determine the distribution of pores. In addition, to obtain pore size distribution in micropore region, the Horvath-Kawazoe (HK) method [16] was applied to the adsorption isotherm using Ar gas for the products.

The powder samples of pillared micas were uniaxially compressed in vacuum at 300 MPa into disk compacts (1.6 × 13ϕ mm) followed by heating in an electric furnace at 500-700 °C for 3 hours in order to obtain sintered bodies. In addition, some sintered bodies were subjected to boring tests using a drill with a diameter of 1.3 mm for the evaluation of machinability.

RESULTS AND DISCUSSION

Figure 1 shows basal spacings and specific surface areas of the alumina-pillared micas heated at 700 °C, plotted against solution loading per 1 g of host crystals. The host micas (solution loading of 0 mmol Al/g mica) gave a basal spacing of 9.6 nm and a specific surface area of 9.7 m^2 g^{-1}. On the other hand, the products, i.e. pillared micas, gave large basal spacings and specific surface areas, indicating that the pillared structure was formed. The products gave different basal spacings and specific surface areas with changing solution loading. Hydroxoaluminum solution contains several cationic Al species, such as Keggin Al_{13} cation and polymeric species of the Al_{13} cation [14]. Selectivity of cationic Al species for cation exchange with interlayer Na^+ ions of host crystals is determined by solution loading. The maximum basal spacing of 2.65 nm and specific surface area of 386 m^2 g^{-1} were observed in the pillared mica prepared under the solution loading of 24 mmol Al/g mica. This indicates that the solution loading is an important parameter to obtain the pillared micas having larger basal spacings and specific surface areas and that the optimal solution loading is 24 mmol Al/g mica in the present study.

Figure 2 shows XRD patterns of the pillared micas heated at different temperatures. The samples were prepared under the solution loading of 24 mmol Al/g mica. The product dried at 60 °C gave (00l) basal reflection assignable to an intercalated compound having the basal spacing of about 3.2 nm. The (001) peak shifted to the higher diffraction angle at 500 °C due to thermal decomposition of PVA in the interlayer regions as well as dehydration and dehydroxylation of intercalated Al species. The pillared micas heated at 500 - 800 °C gave the (001) reflection, showing higher thermal durability of pillared structure than the alumina-pillared micas prepared without using PVA [4].

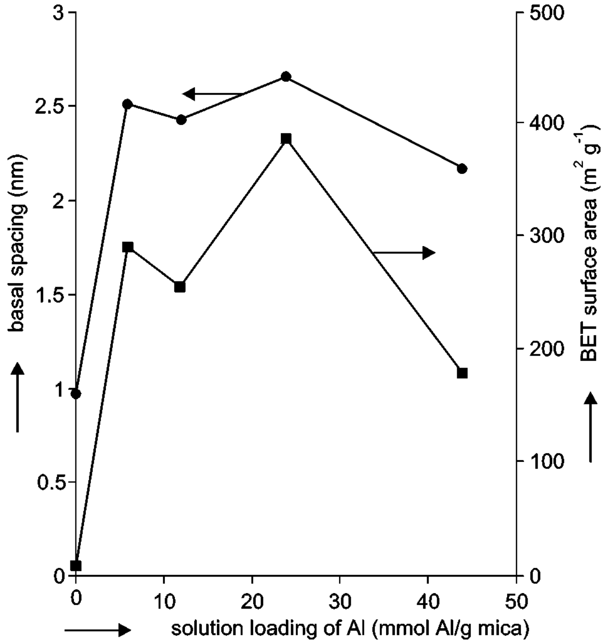

Figure 1. Basal spacing and BET surface area of alumina--pillared micas heated at 700 °C plotted against solution loading per 1 g of host crystals.
● - basal spacing, ■ - BET surface area

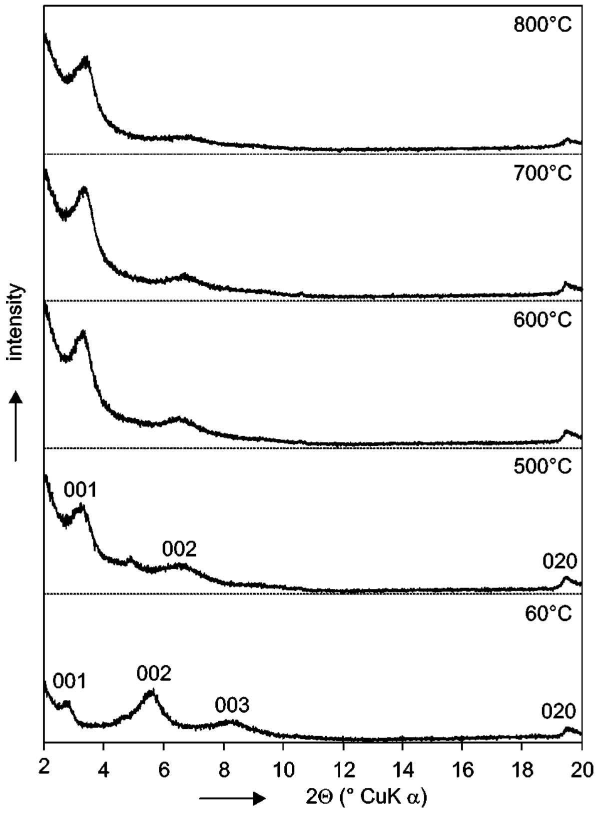

Figure 2. X-ray powder diffraction patterns of alumina-pillared micas heated at different temperatures. Solution loading was 24 mmol Al/g mica.

The product heated at 900 °C lost the (001) reflection, showing collapse of the pillared structure.

Figure 3 shows basal spacings and specific surface areas of the alumina-pillared micas heated at different temperatures. The samples are the same as in figure 2. The basal spacing decreased slightly from 2.7 nm at 500 °C to 2.6 nm at 800 °C. The basal spacings of the products are much larger than those of the alumina-pillared mica prepared without using PVA [4], which gave the basal spacing of 1.8 nm at 500 °C. The larger basal spacings resulted from the increase in intercalation of highly polymerized hydroxoaluminum cations due to the presence of PVA molecules in the interlayer regions of the host micas. This caused a remarkable expansion of the interlayer distance. The nitrogen adsorption isotherms were of BET type. The maximum surface area, 403 m^2 g^{-1}, was obtained at 600 °C. The decrease in surface area of the products heated above 600 °C corresponds to the decrease in the basal spacing of the heated product. The pillared mica had large surface area of above 300 m^2 g^{-1} even after heating at 800 °C, showing high thermal durability.

Figure 4 shows pore size distribution curves for the pillared micas. The pore size distribution curves were obtained by the BJH method [15], which gives the pore size distribution of mesopore and larger pore side of micropore region. The pillared mica samples are the same as in figure 2. The pore size distribution of the host mica crystals heated at 700 °C is also shown in figure 4 for comparison, but the peak is somewhat indistinguishable because of illustrating in the same scale as the pillared micas in the figure. The pillared mica sample gave a peak corresponding to a pore diameter around 3.5 nm. The pores of 3.5 nm resulted from the so-called slit pores, which originated from the regularly interstratified structure of pillared micas. This sort of pores has also been found in Cr_2O_3- [5], Ga_2O_3- [6], TiO_2- [7] and Al_2O_3-pillared fluorine micas [4] reported previously. The shoulders that appear at the smaller diameter sides below 2 nm are observed, illustrating the existence of micropores. The shoulder weakened at 800 °C, corresponding to the decrease in specific surface area as seen in figure 3.

The micropore analysis was undertaken by the *t*-analysis method [17], which gives micropore area and volume, but found to be unsuccessful. Then the HK method [16], which is appropriate for analysis of micropore distribution, was applied to the adsorption isotherm using argon gas. The analysis was done for the pillared mica heated at 600 °C, based on the cylindrical pore model which is applicable to zeolites. The micropore distribution curve showed a peak around 1.9 nm in diameter with the large peak width of about 1.3 nm at half height. This result reconfirms the existence of micropores evaluated by the BJH method above. Although the strict pore geometry is not known for pillared micas, it seems plausible to use the cylindrical pore model for pillared micas.

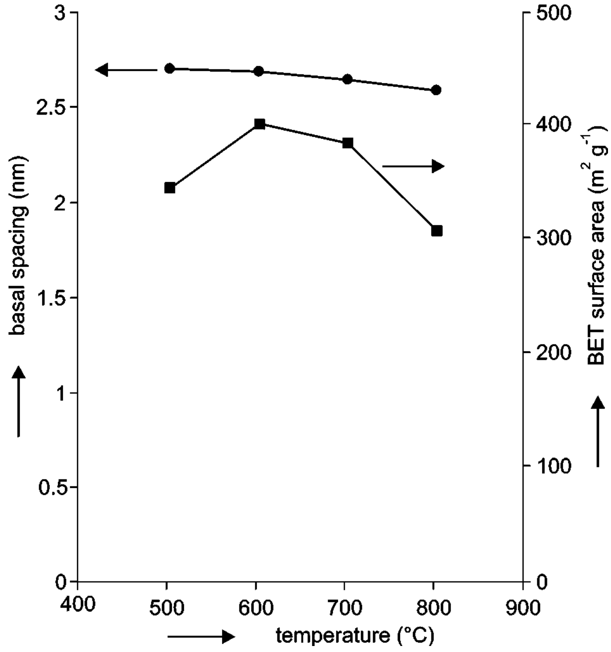

Figure 3. Basal spacing and BET surface area of alumina-pillared micas heated at different temperatures. Solution loading was 24 mmol Al/g mica.
● - basal spacing, ■ - BET surface area

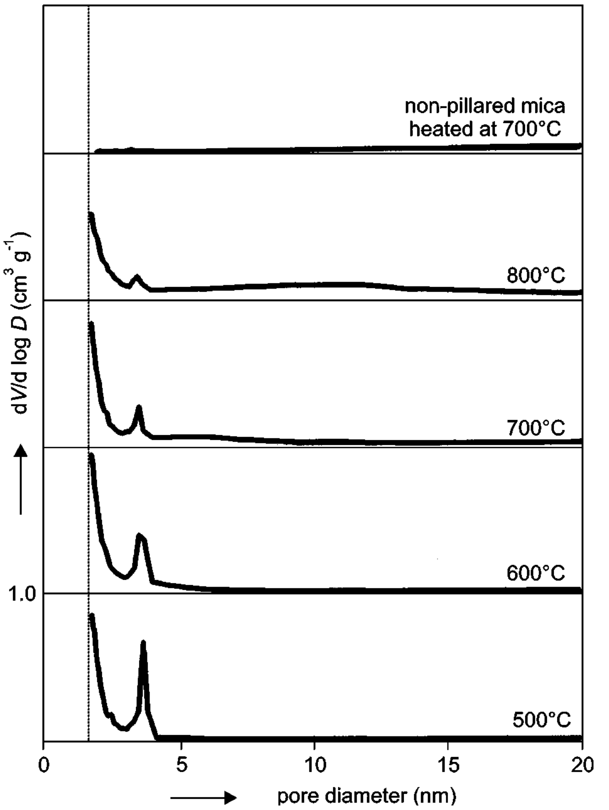

Figure 4. Pore size distribution curves of alumina-pillared micas heated at different temperatures. Solution loading was 24 mmol Al/g mica.

Al contents of the alumina-pillared micas were in the range of 3.5 - 4.3 mol Al per Si_4O_{10} (unit formula of micas). The Al content is rather approximate, because thorough washings after the intercalation process were sometimes unattainable due to the high viscosity of the residual PVA. This may cause the deposition of activated alumina originated from hydroxoaluminum cations onto outer surfaces of the pillared micas when they are calcined. However, the Al contents of the pillared micas obtained in the presence of PVA are substantially larger than those obtained without PVA. This agrees well with the larger clearance space for the pillared micas obtained with PVA. The (001) reflection of the pillared micas remained up to higher temperatures as the solution loading was increased. This indicates that thermal durability of the pillared structure increases with solution loading as a result of increasing pillaring substances, i.e., high pillar density. On the other hand, high pillar density results in a stuffed structure of interlayer regions, which inevitably causes the decrease in pore volumes and surface areas. Thus the appropriate solution loading for obtaining pillared micas is determined by counterbalancing between thermal durability and microporous characteristics.

Sintered bodies of these alumina-pillared micas with longer basal spacings could be also obtained by firing at 500 - 700 °C using pressed powder compacts of the pillared micas. They were machinable and retained porous characteristics. The example of the drilled specimen is shown in figure 5. The good machinability should result from the house-of-cards like micro-structure [4] of the interlocking flakes of cleavable mica crystals. These pillared micas thus obtained are useful due to their sinterability as well as high thermal durability. Cation exchangeabilities for the alumina-pillared micas were observed although their cation exchange capacities were not large. A detailed study on cation exchangeability is underway now and will be reported in the near future.

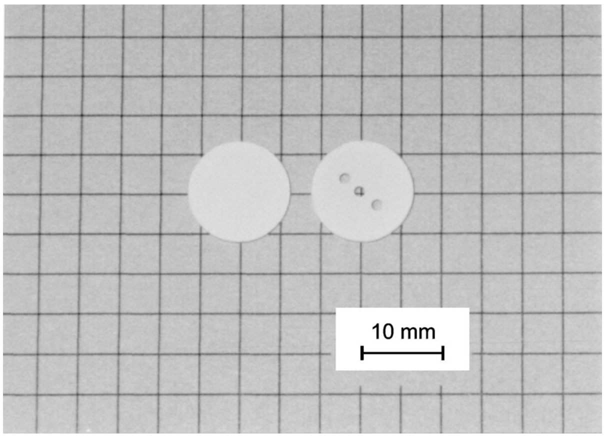

Figure 5. Photograph showing machinability of the sintered body of the alumina-pillared micas.

CONCLUSION

Alumina-pillared fluorine micas were synthesized with different hydroxoaluminum solution loadings under the presence of PVA.

The basal spacings and thermal durabilities of the alumina-pillared micas obtained in the presence of PVA are much larger than those of the alumina-pillared micas obtained without PVA.

The basal spacings and specific surface areas of the alumina-pillared micas depend on hydroxoaluminum solution loadings used for intercalation.

The alumina-pillared micas thus obtained under optimized conditions gave the large basal spacing of 2.7 nm at 500 °C and the maximum surface area of 403 $m^2 g^{-1}$ at 600 °C. The surface area of the product was above 300 $m^2 g^{-1}$ even after heating at 800 °C, showing high thermal durability.

Sintered bodies of the alumina-pillared micas were obtained by firing at 500 – 700 °C using pressed powder compacts of the pillared micas. They were machinable and retained porous characteristics.

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SYNTÉZA ALUMINOU MODIFIKOVANÝCH FLUOROVANÝCH SLÍD S POUŽITÍM POLYVINYLALKOHOLU JAKO ŠABLONY A CHARAKTERISTIKA JEJICH PÓRŮ

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Korundem modifikované fluorované slídy byly připraveny ze syntetické expandovatelné slídy s vysokým mezivrstvým nábojem v různě koncentrovaných roztocích hlinitanu v přítomnosti poly(vinylkaholu) (PVA) s cílem získat mikroporézní látky s vysokou tepelnou stabilitou. Mezirovinné vzdálenosti a specifické povrchy produktů závisejí na koncentraci hlinitanu v roztoku. V této práci byla jako optimální nalezena koncentrace 24 mmol Al na gram slídy. Takto získaný produkt měl značné mezivrstvé vzdálenosti, a to 2,7 nm při 500 °C, a specifický povrch až 403 $m^2\ g^{-1}$ při 600 °C. Specifický povrch produktu byl více než 300 $m^2\ g^{-1}$ dokonce i po zahřátí na 800 °C, což dokazuje značnou tepelnou stabilitu modifikovaných slíd. Distribuce velikosti pórů produktů ukazuje na přítomnost mikropórů. Sintrované objekty z korundem modifikovaných slíd byly získány ze slisovaných prášků kalcinací na 500 - 700 °C. Tyto objekty byly obrobitelné a zachovaly si svůj pórovitý charakter.