EFFECTS OF HOST MICAS, INTERLAYER CATIONS AND THE ADDITION OF PVA ON FORMATION AND POROUS PROPERTIES OF FLUORINE MICA - IRON(III) OXIDE COMPOSITES

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Syntheses of Fe_2O_3 -pillared fluorine micas have been undertaken using Na-tetrasilicic fluorine mica $[NaMg_{2.5}Si_4O_{10}F_2]$, Nataeniolite series mica $[Na_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2]$ and their Li⁺-exchanged forms as host crystals in the presence or absence of PVA as a template agent. The properties and structures of the products depend on the species of host crystals and interlayer cations as well as on the addition of PVA. Fe_2O_3 -pillared fluorine micas obtained from the Li-exchanged form of the taeniolite series mica retained pillared structure up to 600°C and had pores with mean diameter around 3.3 nm. On the other hand, the products obtained from the Li-exchanged form of Na-tetrasilicic mica with using PVA had the "house-of-cards" structure consisting of delaminated Fe_2O_3 -pillared mica flakes and Fe_2O_3 particles deposited on the external surface of the mica flakes. They can be called " Fe_2O_3 pillared mica - Fe_2O_3 " composites which are featured by mesopore distributions in the range of 3.3 - 6.9 nm, depending on the heating temperature. They gave sintered bodies above 500 °C and exhibited a maximum BET specific surface area of 110 m²g⁻¹ at 600 °C.

Keywords: Pillared mica, Fe2O3, Poly(vinyl alcohol), Porous characteristic, Delamination

INTRODUCTION

The intercalation of bulky inorganic polycations into the interlayer region of swelling clay minerals followed by calcination allows the preparation of thermally stable microporous solids, i.e., pillared clays. In pillared clays, the intercalated oxides formed after calcination prop the layers apart as pillars, creating interlayer pores of molecular dimensions. Pillared clays exhibit interesting properties for catalysis, adsorption and separation. Iron oxide pillared clays [1, 2] attract much interest for their use in catalytic reduction of NO by NH_3 [3].

The present authors have focused their attention on expandable synthetic fluorine micas [4, 5] as host crystals for intercalation. These synthetic micas are featured by a 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 [6, 7], chromia-pillared [8], and titania-pillared [9, 10] fluorine micas.

The intercalation of bulky inorganic polycations in hydroxometal solutions by exchanging the chargecompensating cations in the interlayer regions of host crystals depends on the species of host crystals and interlayer cation. In our previous study [6], we showed that the Li⁺-form of the expandable mica tends to intercalate more bulky species than the Na⁺-form of original host micas. The addition of a PVA (poly(vinyl alcohol)) solution prior to intercalation is also effective to intercalate bulky ions. In addition, during preparation of pillared clays, "delaminated clays" [3, 11] are formed depending on the preparation conditions.

In this study, Na-tetrasilicic fluorine mica, $[NaMg_{25}Si_4O_{10}F_2]$ [4], Na-taeniolite series fluorine $[Na_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2]$ [5], mica, and their Li⁺-exchanged forms were used as the host crystals. The aims of this paper are to clarify reaction conditions and porous properties of Fe₂O₃-pillared micas. Especially, the effects of (i) the host mica species, (ii) the interlayer cation species and (iii) the addition of PVA as a template agent on the formation and properties of Fe₂O₃-pillared micas were studied. Sintering of powder compacts of Fe₂O₃-pillared mica was also tried without adding binder. The formation to a specific shape with controlled tolerances and known properties will extend the use of pillared micas.

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EXPERIMENTAL

The starting Na-Tetrasilicic fluorine mica (NaMg_{2.5}Si₄O₁₀F₂; hereafter denoted by Na-TSM) and Na-taeniolite series fluorine mica (Na_{0.5}Mg_{2.5}Li_{0.5}Si₄O₁₀F₂; hereafter denoted by Na-tae) were synthesized by the same procedure as described previously [4, 5]. The maximum dimensions parallel to the layers for both host micas were about 10 μ m while those perpendicular to the layers were about 0.4 μ m. Part of Na-TSM and Na-tae crystals thus obtained were treated by a LiCl solution to exchange interlayer Na⁺ ions into Li⁺ ions to form the Li⁺-saturated forms (hereafter denoted by Li-TSM and Li-tae, espectively). The exchanging ratio of interlayer Na⁺ for Na-TSM and Na-tae is 96 % and 84 %, respectively.

A hydroxoiron(III) solution used as a pillaring agent was prepared by a titration method; a NaOH solution was added to a $FeCl_3$ solution under vigorous stirring. The hydroxoiron(III) solution had an OH/Fe ratio of 2.0 and Fe concentration of 0.066 mol l^{-1} .

The host crystals were dispersed in distilled water with or without adding PVA (the degree of polymerization: 1000) solution and aged at 25 °C for 48 h (hereafter denoted by, for example, Li-TSM-PVA and Li-tae-PVA for the PVA added Li-TSM and Li-tae, respectively). The host suspensions thus obtained were allowed to react with the hydroxoiron solution at 25 °C for 2 h under vigorous stirring followed by aging at the same temperature for 48 h.

The reaction products were separated from the reacted suspensions by vacuum filtration. The collected products were washed with distilled water and then dried in air at 65 °C. The amounts of Fe contained in the products were measured by a gravimetric analysis [12] after the products were fused with Na₂CO₃.

X-ray diffraction (XRD) patterns using CuKa radiation were recorded on the dried samples and the products heated at 400 to 700 °C for 3 h in air. The correction for d-spacings by the internal standard method was not done. BET surface areas and pore size distribution curves of the same samples were evaluated from adsorption-desorption isotherms for N₂ at liquid nitrogen temperature. The BJH method was used to determine the pore distribution curves. Prior to the isotherm measurement, the samples calcined above 200 °C were degassed by evacuation at 200 °C while the samples heated at 65°C were degassed by evacuation at 65 °C. The powder samples of Li-tae and Li-tae-PVA calcined at 65 °C or 400 °C were uniaxially compressed in vacuum at 75 MPa into disk compacts $(1.6 \times 130 \text{ mm})$. They were then heated in air using an electric furnace at 500-700°C for 3 hours in order to obtain fired samples. In addition, some sintered bodies were subjected to boring tests using a drill with a diameter of 1.0 mm for the evaluation of machinability.

RESULTS AND DISCUSSION

Effects of host micas, interlayer cation species and the addition of PVA on the formation of pillared micas

Table 1 shows Fe₂O₃ contents of the products obtained from different host crystals with or without using PVA. The right column in the table shows the Fe content (mol) per unit formula $(/Si_4O_{10})$ of host micas. The Fe₂O₃-pillared mica obtained from Li-tae had larger Fe_2O_3 content than that obtained from Na-tae. This clearly indicates that interlayer cations of host mica crystals have dominant effects on intercalation although the Li⁺-form is not perfectly homoionic. The Fe₂O₃ pillared mica obtained from Li-tae-PVA had slightly larger Fe₂O₃ content than that obtained from Li-tae. This indicates that, for Li-exchanged taeniolite series micas, the addition of PVA leads to intercalation of a large amount of bulky hydroxoiron ions through the preintercalation of PVA molecules into the interlayer regions. On the other hand, the Fe₂O₃ content of the product obtained from Li-TSM-PVA was remarkably large, compared with that obtained from Li-tae-PVA. This difference between Li-TSM-PVA and Li-tae-PVA can be ascribed to the difference in host species. Na-TSM has larger layer charge and cation exchange capacity than Na-tae while both host micas exhibit free swelling. These two host micas also differ in the origin of positive charge deficiency: Negative layer charge of Na-TSM results from octahedral vacancies. The magnitude of layer charge and charge locality determines properties of phyllosilicates [13], causing different behavior of intercalation.

Figure 1 shows XRD patterns of Fe₂O₃-pillared fluorine micas obtained from Li-tae and Li-TSM-PVA heated at different temperatures. The peak at $2\theta = 21.9^{\circ}$ (CuK α) is ascribed to α -cristobalite (SiO₂) as an impurity. The product obtained from Li-tae retained the (001) reflection of 1.26 nm phase [2 θ : 7° (CuK α)] up to 600 °C, while the original Li-tae showed a basal spacing of 0.96 nm at 600 °C. The difference between these basal spacings gives a small clearance space of about 0.3 nm in the interlayer region of the mica but supports the pillaring of oxide because Fe³⁺-exchanged forms have a basal spacing of 0.95 nm. The (001) reflection became weakened at 700 °C. This indicates that the pillared structure of the Fe₂O₃-pillared mica obtained

Table 1. Fe content in the products.

| Sample | Fe_2O_3 (wt.%) | Fe / mol (Si ₄ O ₁₀) ⁻¹ |
|------------|------------------|---|
| Na-tae | 13.0 | 0.83 |
| Li-tae | 25.5 | 1.71 |
| Li-tae-PVA | 28.5 | 1.88 |
| Li-TSM | 20.7 | 1.36 |
| Li-TSM-PVA | 57.7 | 7.88 |



Figure 1. X-ray diffraction patterns for the products obtained from a) Li-tae and b) Li-TSM-PVA upon heating at different temperatures.

• - α -Fe₂O₃, \bigcirc - α -cristobalite

from Li-tae retains up to 600 °C and that the collapse of the pillared structure begins at 700 °C. The reflection lines assignable to α -Fe₂O₃ appeared at 400 °C and became stronger at 700 °C. The precipitation of α -Fe₂O₃ resulted from iron hydroxide deposited on the outer surface of the host micas and the particles of α -Fe₂O₃ grew up with increasing heating temperature. For the sample heated at 700 °C, part of the Fe₂O₃ were expelled onto external surfaces from the interlayer regions of the host crystals, corresponding to the collapse of the pillared structure.

In contrast to the products obtained from Li-tae and Li-tae-PVA, the heated products obtained from Li-TSM-PVA showed no reflections in the 2θ range from 3 to 20° (CuK α). The disappearance of the regular basal reflections and the distinct lines corresponding to larger interlayer spacing was also reported in the preparation of Fe₂O₃-pillared clays [3, 14]. The disappearance of the basal reflection results from delamination of silicate layers in the host crystals. Chen et al [3] described that delaminated pillared clays were formed after long reaction times and at high reaction temperature (40 - 50 °C) using montmorillonite as host crystals. In the present study, the addition of PVA may have led to delamination of mica crystals for the products. Judging from the values of the Fe content (table 1) and the peaks assignable to Fe_2O_3 in XRD patterns, it is concluded that, more or less, Fe₂O₃ particles are deposited on the external surfaces for the Fe₂O₃-pillared micas, especially for the delaminated Fe₂O₃-pillared micas, along with the intercalation into the interlayer regions of host mica crystals. The criterion for intercalation or deposition of the iron oxide precursor on external surfaces becomes more obscure with the promotion of delamination.

Table 2 summarizes sample properties studied. The products obtained from Na-tae, both in the presence and absence of PVA, gave the (001) diffraction peaks

| Sample | Intercalating agents | Delami- nation | Thermal durability | |
|------------|----------------------|-------------------|--------------------|--|
| Na-tae | Iron | No | Below 400 °C | |
| Li-tae | Iron | No | Up to 600 °C | |
| Li-tae-PVA | Iron, PVA | No | Up to 600 °C | |
| Li-TSM | Iron | No | Below 400 °C | |
| Li-TSM-PVA | Iron, PVA | Yes | Up to 700 °C | |

Table 2. Summary of sample properties.

around 9° (Cu $K\alpha$) below 400 °C. This indicates that the collapse of pillared structure occurs at lower temperature, showing relatively low thermal durability. These results indicate that thermal durability of the pillared structure depends on the interlayer cation of the host crystals which affects the selectivity of intercalating species from hydroxoiron solution.

Lithiation of the original host micas also seems to promote intercalation of bulky guest cations and hence the formation of Fe₂O₃-pillared micas with higher thermal durabilities because interalyer Li⁺ ions enhance the degree of swellability. The products obtained from Li-TSM also gave the (001) diffraction around 9° (CuK α) at 400 °C while the product obtained from Li-tae gave the (001) diffraction with a long spacing (1.26 nm) up to 600 °C. The delaminated Fe₂O₃-pillared micas were obtained only from Li-TSM-PVA. Li-tae-PVA produced the Fe₂O₃-pillared micas but did not delaminate. All these facts indicate that the nature of the products depends on the species of host crystals and interlayer cations as well as on the addition of PVA.

Porous properties of the products

Figure 2 shows pore size distribution curves of the products obtained from Li-tae and Li-TSM-PVA heated



Figure 2. Pore size distribution curves for the products obtained from a) Li-tae and b) Li-TSM-PVA upon heating at different temperatures.

at different temperatures. The products obtained from Li-tae heated at 400 - 600 °C gave peaks having a pore diameter of 3.3 - 3.4 nm. This peak is assignable to so-called slit pores, which originate from the interstratified structure of pillared micas. This sort of pores has also been found in chromia- [8], titania- [9] and alumina-pillared fluorine micas [7]. The peak of slit pores was almost in the constant position in the temperature range from 400 to 600 °C and disappeared for the product heated at 700 °C. This corresponds to the thermal collapse at 700 °C mentioned above.

The pore sizes of the product obtained from Li-TSM-PVA at 400 °C has a bimodal distribution, which consist of the slit pore at the pore diameter around 3.3 nm and the broad peak at 4.2 nm. The latter shifted gradually to larger diameter sides as the heating temperature increased, giving a pore diameter of 6.9 nm at 700 °C. This peak originates from the "house-ofcards" structure [15] of delaminated pillared mica flakes, and corresponds to the same type of pore distribution for delaminated titania-pillared micas [10]. The interlocking voids formed in the house-of-cards structure may extend gradually with increasing heating temperature due to the segregation and grain growth of Fe₂O₃ particles deposited on the outer surfaces of delaminated mica flakes.

Figure 3 shows specific surface area *a*) and total pore volume *b*) of the products obtained from Li-tae, Li-tae-PVA and Li-TSM-PVA heated at different temperatures. Specific surface areas for both original micas of Na-tae and Na-TSM were about $4 \text{ m}^2 \text{ g}^{-1}$ in the temperature range of 25 to 700 °C. BET surface area of the pillared mica obtained from Li-tae decreased at

300 °C, and then slightly increased at 400°C to 76 m² g⁻¹, retaining almost constant values in the temperature range between 400 °C and 600 °C. The abrupt decrease in the surface area was observed for the product obtained from Li-tae at 700 °C, corresponding to the collapse of the pillared structure described above. Surface areas of Li-TSM-PVA also decreased at 300 °C, and then increased with increasing heating temperature up to 600 °C, showing a maximum value of ca. 110 m² g⁻¹, and decreased again at 700 °C. The decrease in the surface area of the product obtained from Li-TSM-PVA at 700 °C may result from the collapse of pillared structure in the matrix of the delaminated microstructure. The steep increase in the surface area of the product obtained from Li-tae-PVA at 400 °C is probably attributed to thermal decomposition of PVA in the interlayer regions although intercalated PVA molecules does not burn out completely at this temperature. Thermal decomposition behavior of PVA molecules seems to differ between the interstratified structure of the Li-Tae-PVA sample and the delaminated microstructure of the Li-TSM-PVA sample.

The total pore volumes of the products obtained from Li-tae and Li-tae-PVA increased above 300 °C and attained the almost constant value of 0.14 and 0.17 cm³ g⁻¹, respectively. The product obtained from Li-TSM-PVA also shows similar thermal changes, however, it shows the highest total pore volume among the samples studied. This can be attributed to the delaminated microstructure, which causes the formation of large-size mesopores through the course of PVA decomposition upon heating. The values of total pore volume of the product obtained from Li-TSM-PVA, i.e., the delami-



Figure 3. *a*) BET specific surface area and *b*) total pore volume plotted against heating temperature for the products. \blacktriangle - Product obtained from Li-tae, \Box - Product obtained from Li-tae -PVA, \bullet - Product obtained from Li-TSM-PVA.



Figure 4. Optical photograph of sintered bodies obtained from Li-tae.

nated Fe_2O_3 -pillared mica, were in the same magnitude with the delaminated titania-pillared micas [10].

Considering the large amount of Fe_2O_3 (table 1) for delaminated Fe_2O_3 -pillared micas, they can be called as "Fe₂O₃ pillared mica - Fe₂O₃" composites, which are featured by monomodal mesopore distributions. The interlocking silicate layer of delaminated micas probably hinder the particle growth of Fe_2O_3 , which is segregated from the outer surfaces of silicate layers upon heating. This results in a monomodal mesopore distribution at 600 - 700 °C.

Sintered bodies of Fe_2O_3 -pillared micas were obtainable by pressing and firing at 500 °C for 3 h and were found to be machinable. The example of the drilled specimen obtained from Li-tae is shown in figure 4. The good machinability should result from cleavability of mica flakes and the microstructure featured by the house-of-cards structure. Sintered bodies also retain porous properties shown in figures 2 and 3 as far as the products obtained at 65 °C are used for sintering.

CONCLUSION

Syntheses of Fe_2O_3 -pillared fluorine mica have been undertaken using Na-tetrasilicic fluorine mica, Na-taeniolite series fluorine mica and their Li⁺-exchanged forms as host crystals in the presence or absence of PVA as a template agent. The effects of host crystal species, interlayer cations and the addition of PVA on the nature and structure of the products were investigated. The results are summarized as follows:

- The properties and structure of the products depend on the species of host crystals and interlayer cations as well as on the addition of PVA. Composites having Fe₂O₃-pillared structure and/or delaminated Fe₂O₃-pillared structure are formed upon heating. They are featured by monomodal mesopore distributions.
- Fe₂O₃-pillared micas obtained from Li-tae retain the pillared structure up to 600 °C. Li⁺-exchanged forms of the host mica crystals are indispensable for obtaining Fe₂O₃-pillared micas having higher thermal durabilities.

 The products obtained from Li-TSM-PVA had the "house-of-cards" structure consisted of delaminated Fe₂O₃-pillared mica flakes and Fe₂O₃ deposited on the external surfaces of the mica sheets. They can be called as "Fe₂O₃ pillared mica - Fe₂O₃" composites which are featured by monomodal mesopore distributions in the range of 3.3 - 6.9 nm.

References

- 1. Yamanaka S., Doi T., Sako S., Hattori M.: Mater. Res. Bull. *19*, 161 (1984).
- 2. Rightor E. G., Tzou M-S., Pinnavaia T. J.: J. Catal. *130*, 29 (1991).
- 3. Chen J. P., Hausladen M. C., Yang R. T.: J. Catal. *151*, 135 (1995).
- Kitajima K., Daimon N.: Nippon Kagaku Kaishi 991 (1975).
- Kitajima K., Koyama F., Takusagawa N.: Bull. Chem. Soc. Jpn. 58, 1325 (1985).
- 6. Fujita T., Kitajima K., Taruta S., Takusagawa N.: Nippon Kagaku Kaishi 1123 (1993).
- 7. Yamaguchi T., Sakai Y., Kitajima K.: J. Mater. Sci. *34*, 5771 (1999).
- 8. Yamaguchi T., Matsukura S., Fujita T., Takusagawa N., Kitajima K.: Nippon Kagaku Kaishi 862 (1997).
- Kitajima K., Kuniyoshi F.: Solid State Ionics 101-103, 1099 (1997).
- Yamaguchi T., Kuniyoshi F., Kitajima K.: J. Mater. Sci. 34, 3685 (1999).
- Pinnavaia T. J., Tzou M-S., Landau S. D., Raythatha R.: J. Mol. Catal. 27, 195 (1984).
- 12. Shimoda S.: Nendo Koubutu Kenkyuhou (Methods of Clay Minerals Investigation), p.24-30, Souzousya, Tokyo 1985.
- Bailey S. W. in: *Reviews in Mineralogy 19, Hydrous Phyllosilicates*, p.1-8, Mineralogical Society of America, Michigan 1988.
- 14. Burch R., Warburton C. I.: J. Chem. Soc., Chem. Commun. 117 (1987).
- Beall G. H. in: Hench L. L., Freiman S. W. Eds., Advances in Nucleation and Crystallization in Glasses, p.251. American Ceramic Society, Ohio 1972.

VLIV HOSTUJÍCÍCH SLÍD, MEZIROVINNÝCH KATIONTŮ A PŘÍDAVKU POLYVINYL ALKOHOLU NA TVORBU A PÓROVITOST KOMPOZITŮ FLUOROVANÝCH SLÍD A OXIDU ŽELEZITÉHO

TOMOHIRO YAMAGUCHI*, SHUNSUKE IIDA, KUNIO KITAJIMA

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan Fluorované slídy byly modifikovány oxidem železitým s použitím sodnokřemičité fluorované slídy [NaMg_{2.5}Si₄O₁₀F₂], řady slíd na bázi Na-taeniolitu [Na_{0.5}Mg_{2.5}Li_{0.5}Si₄O₁₀F₂] a jejich Li forem, v některých případech v přítomnosti polyvinylalkoholu (PVA). Vlastnosti a struktura produktů závisí na druhu slídy, kationtů v mezivrstvách a přídavku PVA. Fluorované slídy modifikované oxidem železitým získané z Li formy taeolinitové řady si zachovaly až do 600 °C novou strukturu s póry o velikosti přibližně 3,3 nm. Produkty získané z Li forem sodnokřemičitých slíd za přítomnosti PVA měly strukturu "domečku z karet" tvořenou delaminovanými šupinkami slíd modifikovaných Fe_2O_3 a částic Fe_2O_3 na jejich vnějším povrchu. Tuto struktura je kompozitem slídy modifikované Fe_2O_3 a Fe_2O_3 s velikostí pórů 3,3 - 6,9 nm v závislosti na teplotě ohřevu. Kompozity se nad 500 °C slinují a specifický povrch dosahuje maxima 110 m² g⁻¹ při 600 °C.