Silylation of layered zirconium hydroxy phosphate and its porous properties

**Takahiro Takei · Yoshinori Yonesaki ·
Nobuhiro Kumada · Nobukazu Kinomura**

© Springer Science+Business Media, LLC 2007

Abstract Silylation of layered zirconium hydroxy phosphate was carried out and its porous properties were examined. The novel layered hydroxy phosphate was protonated and intercalated by using octylamine to expand the interlayer space. Then, dimethyldichlorosilane, dichloromethylvinylsilane or 1,2-bisdimethylchlorosilylethane were used to silylate the interlayer space. In order to form micropores between layers, the silylated compounds were heated at the range from 100 °C to 1,000 °C to measure high-temperature XRD patterns. During heating, the interlayer spacing decreased at around 300 and 600–700 °C. The specific surface area reached around 180 m^2/g as maximum area at 300 °C, while layered structure collapsed gradually above 400 °C. Micropore volume also became maximum at 300 °C.

Introduction

Many researchers are interested in inorganic layered materials as hosts for various guests [1–4] and nanosheets via exfoliation [5–8]. Mainly, three kinds of layered material have been examined as host material or nanosheet. Those are; layered perovskites, metal phosphates and clay compounds [1, 3, 5]. The host materials are investigated for use of inorganic-organic hybrid, porous material, ion exchanging material [1–4, 7–4, 9] and so on. On the other hand, the nanosheets are examined for preparation of thin film, novel layered structure and other unique structures [2, 7, T. Takei et al. submitted].

Especially, layered metal phosphates are seen as candidates for host materials for organic molecules and various ions due to their good intercalation and ion exchange properties [9]. The layered zirconium phosphate has two kinds of structure, α and γ-zirconium phosphate [10–12]. Since α-zirconium phosphate especially has high reactivity, ion-exchangeability and intercalation property, it is very interesting and has been studied by many researchers [8, 13–17]. On the other hand, we reported a new layered zirconium hydroxy phosphate, synthesized by hydrothermal reaction [18]. Compared with α-zirconium phosphate, this novel layered phase differs as following. While H$_2$O molecules exist in the interlayer space of α-zirconium phosphate, ethylenediammonium and inorganic ammonium cations are located in the space of the novel zirconium hydroxy phosphate. The P/Zr ratio is 2 and 4/3 for the α-zirconium phosphate and the novel zirconium hydroxy phosphate, respectively.

We examined the ion exchangeability and intercalation property of the novel zirconium hydroxy phosphate [19]. The Ag$^+$ and H$^+$ ions were found to be exchangeable for ethylenediammonium or inorganic ammonium cations. The protonated zirconium hydroxy phosphate could be intercalated by alkylmonoamine via acid–base reaction in the presence of ethylamine as an exfoliator. Since the interlayer spaces are expanded by intercalated molecules, the intercalated layered compound can be used for formation of micropore

T. Takei (✉) · Y. Yonesaki · N. Kumada · N. Kinomura
Center for Crystal Science and Technology, Faculty of
Engineering, University of Yamanashi, 7 Miyamae,
Kofu, Yamanashi 400-8511, Japan
e-mail: takei@yamanashi.ac.jp

between inorganic layers. In this paper, silylation of inorganic layer of the intercalated compound was performed to synthesize microporous material and its thermal behavior was examined.

Experimental

Synthesis of layered zirconium hydroxy phosphate

Synthesis of starting material was carried out by the process reported [18]. Zirconium oxychloride octahydrate ($ZrCl_2O \cdot 8H_2O$) was dissolved in ethylene glycol with stirring and phosphoric acid was added into this solution. Then, ammonium fluoride and ethylenediamine were put into the mixed solution under vigorous stirring. The resulting solution was poured into a Teflon-sealed vessel and hydrothermally treated at 180 °C for 96 h. After the hydrothermal reaction, the aggregates were separated and washed by water via suction filtration using an aspirator, and then dried at 55 °C for 24 h. The chemical formula of $(NH_4)_2(enH_2)_2[Zr_3(OH)_6(PO_4)_4]$ (en: ethylenediamine) and the crystal structure of the product has already been determined by single crystal X-ray diffraction [18]. It is designated as [ZrH-P] hereafter.

The [ZrH-P] was protonated by hydrochloric acid aqueous solution with 0.5 mol/L. The [ZrH-P] was put into HCl aqueous solution and was shaken at 40 °C for 72 h, separated by filtration and washed by distilled water. By this treatment, parts of NH_4^+ and enH_2^{2+} were exchanged with H^+ in the interlayer space of [ZrH-P]. Hereafter, it is designated as H^+[ZrH-P].

Intercalation and silylation

The octylamine intercalation was examined with ethylamine as an exfoliator. The H^+[ZrH-P] was put into an octylamine aqueous solution in the proportion of 0.85 g of the H^+[ZrH-P] to 40 mL of the solution which contained ethylamine as the exfoliator. The molar ratio of the H^+[ZrH-P], octylamine and ethylamine was 1:2:1. The samples were kept airtight at room temperature for 24 h, separated by centrifugation and then dried at RT.

The intercalated intermediate was then silylated using 1,2-bis dimethylchlorosilylethane ($((CH_3)_2ClSi)_2C_2H_4$, BMCE), dichloromethylvinylsilane ($Cl_2(CH_3)(CH_2CH)Si$, DCMV) or dimethyldichlorosilane ($(CH_3)_2Cl_2Si$, DMDC). The organic silane and intercalated intermediate were put into dehydrated toluene solution with the molar ratio of 5 to 1 in a glove box filled with dried N_2 gas. The mixed solution was then refluxed at 50 °C for 24 h with bubbling of dried N_2

gas. The consequent sample was centrifuged three times with toluene and was dried at 55 °C. During the silylation treatment, octylamine cations reacted with chloride anions to form water-soluble amine hydrochloric salt confirmed via XRD patterns. Therefore, the resulting sample was washed with H_2O and dried again in order to dissolve the unwanted salt and obtain the final silylated sample. Hereafter, they are designated as BMCE5, DCMV5 and DMDC5, respectively. In order to investigate thermal behavior of their porous properties by structural reconstruction, BMCE5, DCMV5 and DMDC5 were heated at 200, 300, 400 and 500 °C for 1 h using a box type electric furnace.

Characterization

The layered structure of the silylated samples was estimated by powder XRD (MXP^3, Mac Science) using Ni filtered monochromatic CuKα radiation. The thermal change of interlayer spacing was examined by high-temperature XRD (RINT 1100, Rigaku) using monochromatic CuKα radiation between 100 °C and 1,000 °C. The samples were examined by thermogravimetry, differential thermal analysis (TAS200, Rigaku) and infrared-ray spectroscopy (FT-IR, FT/IR-410, Jasco). The organic elements included in the samples were estimated by CHN elemental analysis (MT-5, Yanaco), while the amount of Si which inserted into the interlayer space on silylation was estimated by inductively coupled plasma emission spectroscopy (P4010, Hitachi).

Results and discussion

Chemical composition of silylated [ZrH-P]

Figure 1 shows the XRD patterns of samples protonated, intercalated and silylated [ZrH-P]. The d_{001}-spacing of around 0.74 nm for the starting material was expanded by protonation to around 0.82 nm and by intercalation of octylamine molecules to around 2.76 nm. For the intercalated compound, bilayer texture was found to be formed by the octylamine in the interlayer space. In the XRD patterns of the silylated compounds with BMCE and DMDC, bimodal peaks were observed and the main d-spacings were around 2.57 and 2.58 nm, respectively. In the case of DCMV, the spacing of around 2.58 nm was obtained. The decrease of the interlayer spacing during silylation was plausibly caused by the partial removal of the octylamine molecules. After the silylation, the amine molecules tilted more or the structure changed from bilayer to monolayer upon their removal.
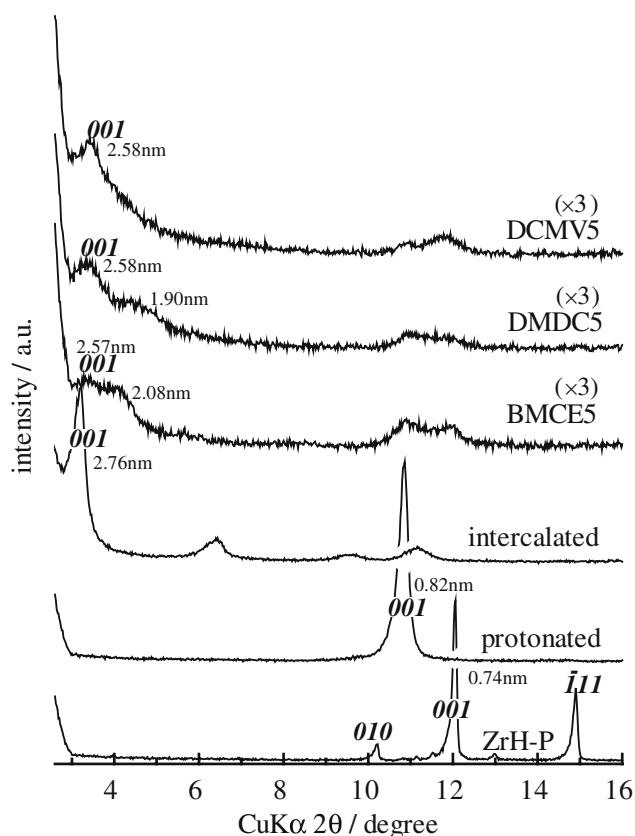
Fig. 1 XRD patterns of starting material, protonated, intercalated and silylated compounds

Fig. 2 TG curves of the silylated compounds

Figure 2 shows the TG curves of the silylated compounds from 20 °C to 1,000 °C. Below 200 °C, adsorbed H_2O was released. In the temperature range from 200 °C to 600 °C, the sample weights decreased gradually with increasing temperature and were constant above 600 °C. These decreases indicate that the intercalated octylamine and silane molecules decomposed gradually. The consequent weight losses of DMDC5 and DCMV5 were around 40 mass%, respectively, whereas that of BMCE5 was around 50 mass%. In order to confirm the chemical formulas of silylated compounds, ICP measurements were carried out. First, we checked the composition of H^+[ZrH-P]; its actual composition formula was found to be $(NH_4)_{0.37}(enH_2)_{0.80}H_{4.03}[Zr_3(OH)_6(PO_4)_4]$. Supposing that amounts of NH_4^+ and enH_2^{2+} are constant via intercalation and silylation treatments, the general formula of the silylated [ZrH-P] can be expressed as follows:
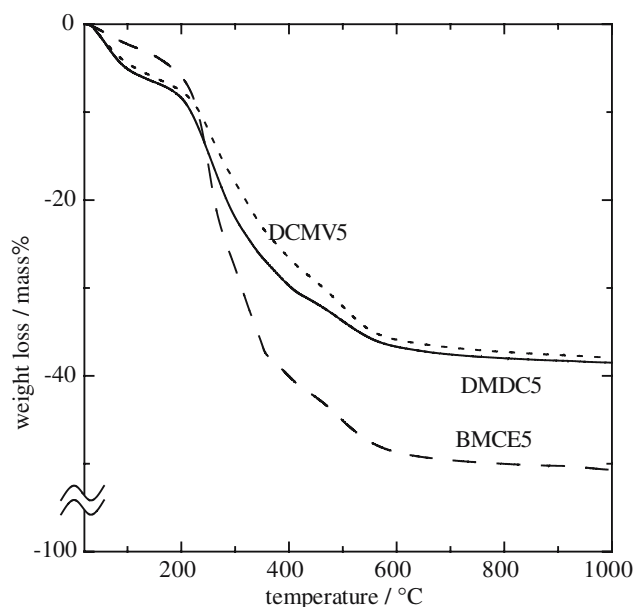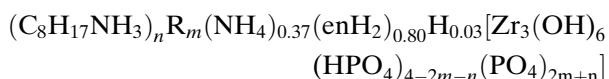
$$(C_8H_{17}NH_3)_n R_m (NH_4)_{0.37}(enH_2)_{0.80}H_{0.03}[Zr_3(OH)_6$$
$$(HPO_4)_{4-2m-n}(PO_4)_{2m+n}]$$

where n and m indicate amount of intercalated octylamine and silane molecules in a formula unit of silylated [ZrH-P], respectively. R indicates the moiety of the dechlorinated silane molecules. Table 1 shows parameters, n and m, of their chemical formula, d_{001}-spacings and fractions of bounded P with silane molecule, m/P.

The silane molecules used in this paper have two Cl atoms. Since one Cl can bond one hydroxyl group in HPO_4, one silane molecule bridges theoretically to two HPO_4. Therefore, the theoretical maximum value of m can be presumed as 2. In the case of the number of intercalated amine molecules, an n of 3.68 was calculated for the intercalated compound. After silylation treatment, n decreased toward 1.12–2.19. This decrease can be considered to be due to replacement of intercalated octylamine with silane molecules during the silylation treatment. In the case of BMCE5, the

Table 1 Chemical formulae of the silylated compounds

Compound	Chemical formula		d_{001}/nm	m/P
	n	m		
Protonated [ZrH-P]	0.00	0.00	0.80	0.00
Intercalated	3.68	0.00	2.80	0.00
Silylated				
BMCE5	2.19	0.62	2.21	0.16
DMDC5	1.12	0.88	2.55	0.22
DCMV5	1.43	1.26	1.88	0.32

largest amount of octylamine and the smallest amount of silane molecules were included.

Thermal behavior of silylated compounds with layered structure

In order to consider the dependence of the interlayer spacing on heating temperature, high-temperature XRD patterns of the silylated compounds were measured at the temperature range from RT to 1,000 °C. The dependence of d_{001}-spacing on temperature is shown in Fig. 3. In these plots, diffraction angles of the bimodal peaks in DMDC5 and BMCE5 were determined from center of gravity of the bimodal peak regarded as one peak.

The interlayer spacings of DMDC5 and DCMV5 were about 2.6 nm at RT, and decreased steeply at around 300 °C to be about 1.5 nm at 400 °C. The interlayer spacings remained constant at the temperature range from 400 to 600 °C and decreased again to around 1.0 nm at 700 °C or higher. Thus, three plateaus exist, designated as 1st, 2nd and 3rd stages. Their stages seem to be akin to the change of silylated α-ZrP (T. Takei et al. submitted). At the 1st stage at RT, the intercalated amines coexist with silane molecules are interleaved between inorganic layers. At the 2nd stage, the anime molecules are removed to decrease the interlayer spacing. Organic groups in the silane molecules are partially decomposing at this stage. At the 3rd stage, the silane molecules are completely oxidized to form SiO_2.
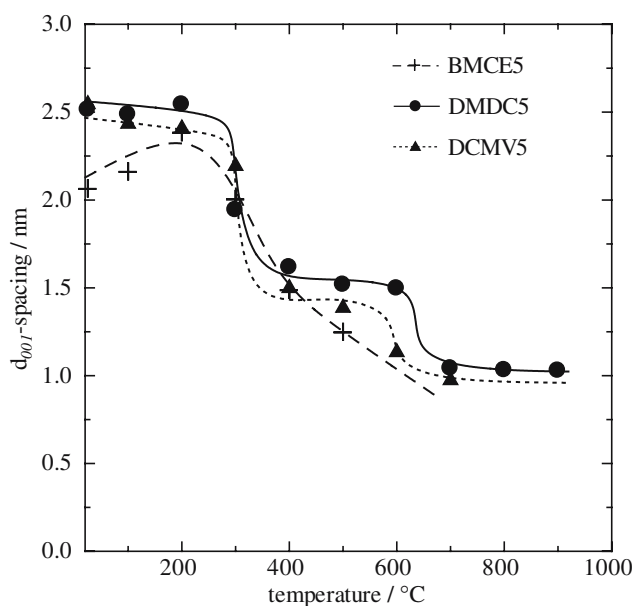
For BMCE5, the spacing was around 2.0 nm at RT, somewhat increased up to 200 °C and decreased above 200 °C. The gradual decrease can be considered to indicate the deformation of the layered structure due to the small amount of silylated BMCE as mentioned in detail in the follow section.

Porous properties

Figure 4 shows relationships between heating temperature and the specific surface area on the lower half and X-ray integrated intensity of the 001 diffraction peaks on the top half of the graph. In the case of BMCE5, the surface area reached a maximum of around 75 m^2/g at 200 °C and decreased gradually upon increased temperature. The peak intensity became maximum at 300 °C and then decreased. These dependences correspond to the deformation of the layered structure as mentioned in the previous section. For DCMV5 and DMDC5, the surface areas
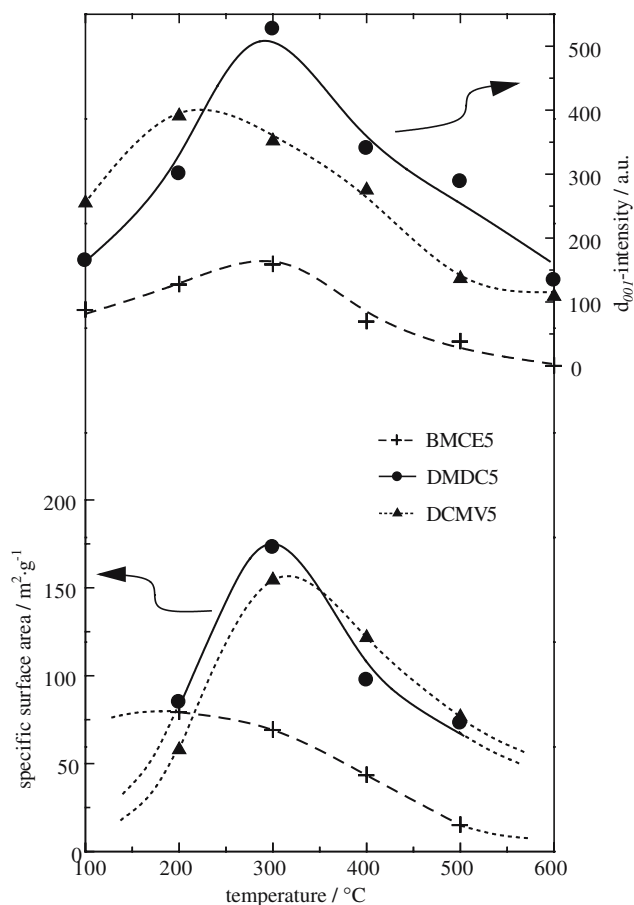

Fig. 3 Relationship between heating temperature and d_{001}-spacing of silylated compounds

Fig. 4 Dependence of specific surface area and d_{001}-intensity of XRD patterns on heating temperature

increased steeply at 200–300 °C to around 154 and 173 m^2/g, respectively, and decreased at higher temperature. At 500 °C, surface areas of the DCMV5 and DMDC5 decreased to around 75 m^2/g. The 001 intensities of DMDC5 and DCMV5 have similar tendencies to their surface areas. The decreases of 001 intensity show the partial collapse or disappearance of layered structure, that is, pores between inorganic layers disappear partially to decrease their surface areas. The difference of the surface area between BMCE5, and DMDC5 and DCMV5 can be considered as due to the amount of silane molecules in BMCE5 being smaller than those in DMDC5 and DCMV5.

Figure 5 shows the pore size distributions for mesopores of these silylated samples calculated by the DH method. Mesopores with around 2 nm of radius are confirmed to exist in all samples. Pore size distributions peaks of the three kinds of silylated compounds are very similar for samples heated at 200 °C, while those differ each other according to silylated compounds heated at higher temperature. In the case of BMCE5, for pores larger than 1.5 nm, the size distribution was hardly changed via heating. However, in the cases of DCMV5 and DMDC5, the height of the distribution peak around 2 nm apparently increased by heating at 300 °C and was constant by heating above 400 °C. On the other hand, the number of pores smaller than 1.5 nm increased by heating at 300 °C and decreased as the heating temperature was raised, while pores larger than 2.2 nm increased gradually with heating temperature within the range from 200 °C to 500 °C.

Volumes of micro and mesopores were estimated by t-plots of each sample showed in Fig. 6. Almost all t-curves of heated samples have similar tendencies to vary their slopes at ≈0.6 nm in t, indicating the existence of the micropores with ≈ 0.6 nm in radius. Generally, the volume of the micropores can be estimated from the intercept of the tangent line contacting the plots in the large t region. From these t-plots in Fig. 6, heated DCMV5 and DMDC5 are found to have larger amount of micropore volume than heated BMCE5. Dependence of the volumes of the micro and mesopores of the silylated samples on heating temperature are shown in Fig. 7. The total pore volumes were estimated from these isotherms at the relative pressure of 0.963 which was corresponding to pore size of 50 nm in diameter via the Kelvin formula. From Fig. 7, the total pore volume of around 0.07 mL g^{-1} in BMCE5 gradually decreased with increase of heating temperature, while in DCMV5 and DMDC5 pore volumes increased up to 300 °C and were constant at around 0.17 and 0.15 mL g^{-1} above 300 °C, respectively. In the case of the micropores, the volume of around 0.04 mL g^{-1} for BMCE5 gradually decreased with temperature, while those for DCMV5 and DMDC5 reached the maximum value of around 0.08 mL g^{-1} at 300 °C and decreased at higher heating temperature. On the other hand, the volume of the mesopores did not change in BMCE5, while in DCMV5 and DMDC5 increased with heating temperature. Mesopores with radii of 2 nm are assigned not to interlayer spaces but to cavities between primary

Fig. 5 Pore size distributions of silylated compound heated at 200–500 °C

Fig. 6 Relationship between t and adsorption volume of silylated compound heated at 200–500 °C

Fig. 7 Relationship between heating temperature and pore volumes of silylated compounds heated at 200–500 °C
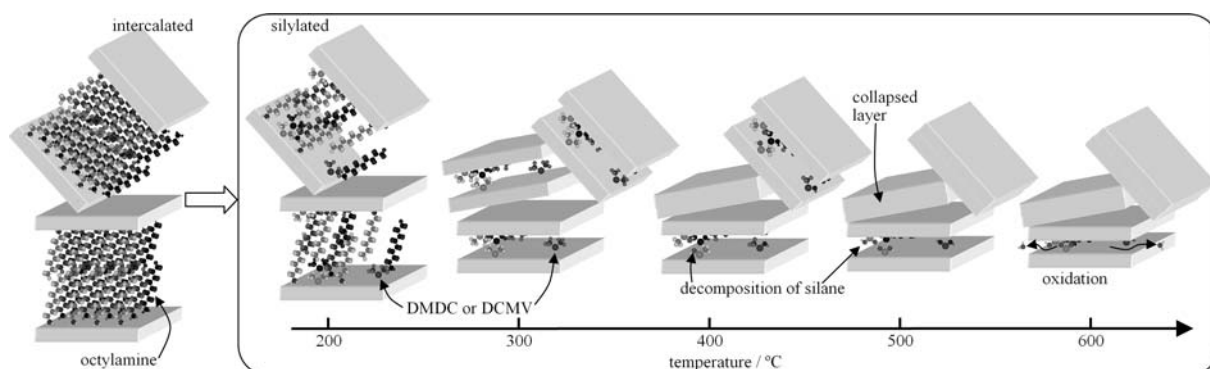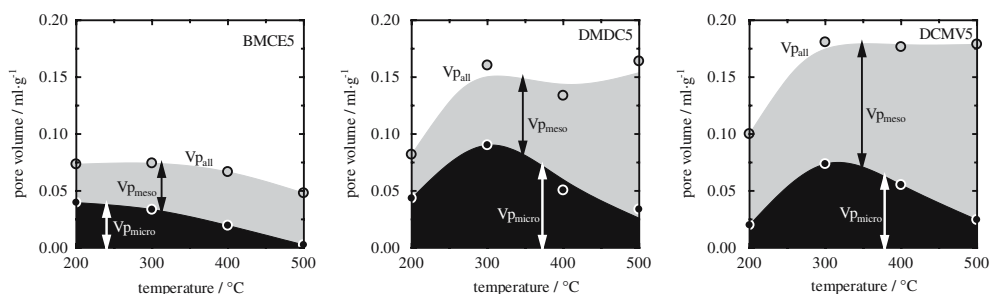

Fig. 8 Schematic illustration of the thermal behavior of the silylated compounds

particles, and those with radii larger than 2.2 nm are assigned to cavities between secondary particles. Although the reason of the increase of the mesopores larger than 2.2 nm is unaccountable at this time, it contributes to the increase of mesopore volume at >300 °C in Fig. 7 as if it compensates for the decrease of micropores. As shown in Figs. 4 and 7, the specific surface area changed in accordance with the change of micropore.

Upon considering the transformation of the layered structure and the changes of porosity, the thermal behavior of the DMDC5 or DCMV5 could be expressed as shown in Fig. 8. Under 200 °C, designated as the 1st stage, the intercalated amines coexist with silane molecules are interleaved between inorganic layers as aforementioned. The intercalated amine molecules are released from silylated compounds at the temperature range from 200 °C to 300 °C and micropores are formed in their place. Silane molecules are partially decomposed above 300 °C within the 2nd stage and are oxidized at 600 °C to form inorganic SiO_2 components. This concluding state was named as the 3rd stage as above. On the other hand, the layered structure has begun to collapse above 400 °C. This collapse gave rise to deterioration of micropores which decreased the surface area. The formation and disappearance of micropores caused the specific surface area to attain maximum at 300 °C. In the case of BMCE5, larger

amounts of the octylamine and smaller amounts of the silane were intercalated than the others as showed in Table 1. The small amount of silane could not sustain the layered structure after release of the octylamine. Therefore, the interlayer spacing gradually decreased without plateaus depending on heating temperature.

Conclusions

Silylation of layered zirconium hydroxy phosphate was performed and its porous properties were examined with the following results.

1. The interlayer spacing of silylated [ZrH-P] decreased at around 300 and 600–700 °C and three plateau regions emerged. The spacing was around 2.5, 1.5 and 1.0 nm below 300 °C, 400–600 °C and above 700 °C.
2. The [ZrH-P] became porous by silylation reactions with DMDC and DCMV, while that have low surface area by silylation with BMCE.
3. In the case of the silylated compounds with DMDC and DCMV, the maximum specific surface area and the volume of the micropore reached around 180 m^2/g and 0.10 mL/g at 300 °C, respectively.
4. The layered structure started collapsing by heating above 400 °C.

References

1. Zampronio EC, Oliveira HP (2004) Mater Res Bull 39:1525
2. Sumida T, Takahara Y, Abe R, Hara M, Kondo JN, Domen K, Kakihana M, Yoshimura M (2001) Phys Chem Chem Phys 3:640
3. Bortun AI, Khainakov SA, Bortun LN, Jaimez E, García JR, Clearfield A (1999) Mater Res Bull 34:921
4. Li B, Hu Y, Zhang R, Chen Z, Fan W (2003) Mater Res Bull 38:1567
5. Ebina Y, Sasaki T, Watanabe M (2002) Solid State Ionics 151:177
6. Bizeto MA, Constantino VRL (2004) Mater Res Bull 39:1811
7. Wang J, Yin S, Sato T (2004) Chem Lett 33:1104
8. Kaschak DM, Johnson SA, Hooks DE, Kim H-N, Ward MD, Mallouk TE (1998) J Am Chem Soc 120:10887
9. Alberti G (1978) Acc Chem Res 11:163
10. Christensen AN, Andersenek EK, Andersen IGK, Alberti G, Nielsen M, Lehmann MS (1990) Acta Chem Scand 44:865
11. Nakayama H, Eguchi T, Nakayama N, Yamaguchi S, Danjo M, Tsuhako M (1997) J Mater Chem 7:1063
12. Clearfield A, Smith G (1969) Inorg Chem 8:431
13. Kinomura N, Fukutomi Y, Kumada N, Suzuki T (1999) Phos Res Bull 10:189
14. Alberti G, Constantino U, Allulli S, Tomassini N (1978) J Inorg Nucl Chem 40:1113
15. Clearfield A (1988) Chem Rev 88:125
16. Kim H-N, Keller SW, Mallouk TE (1997) Chem Mater 9:1414
17. Raveau B (1987) Rev Inorg Chem 9:37
18. Wang D, Yu R, Kumada N, Kinomura N (2000) Chem Mater 12:956
19. Takei T, Sekijima K, Kumada N, Kinomura N (2004) Solid State Ionics 170:111