Synthesis of a Microporous Layered Titanium Phenylphosphonate in Presence of Sodium Dodecylsulfate

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ドデシル硫酸ナトリウム存在下でのミクロポーラスな層状フェニルリン酸チタンの合成

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Microporous layered titanium phenylphosphonate, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5)_2$ and sulfonated titanium phenylphosphonate, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.89}(\text{O}_3\text{PC}_6\text{H}_5)_{1.1} \cdot 1.8\text{H}_2\text{O}$ were prepared in the presence of sodium dodecylsulfate (SDS). Interplanar spacing (d_{001}) of titanium phenylphosphonate is 1.43 nm and after sulfonation it increased to 1.64 nm. The surface area of titanium phenylphosphonate is $264 \text{ m}^2 \text{ g}^{-1}$.

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1. Introduction

Following the discovery of layered zirconium phenylphosphonate, $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$, in 1978¹⁾ and after the determination in 1993²⁾ that its structure is similar to that of α -zirconium phosphate, $[\text{Zr}^{\text{IV}}(\text{O}_3\text{P}-\text{OH})_2 \cdot \text{H}_2\text{O}]$ or $[\text{M}^{\text{IV}}(\text{O}_3\text{P}-\text{R})_2 \cdot \text{solvent}]$ (where R = alkyl, aryl, alcoholic, amino, carboxylic, sulfonic, etc., and solvent are intercalated molecules, when present), the chemistry of layered metal (IV) phenylphosphonate, $\text{M}^{\text{IV}}[(\text{O}_3\text{PC}_6\text{H}_5)_2]$ was greatly extended (studied).^{1)–9)} Recently, the nonhydrolytic sol-gel route was reported as effective in the preparation of layered M (IV) phenylphosphonates (where M = Si, Zr, Ti and Sn) and no information of porosity was provided.¹⁰⁾ Organic derivatives of γ -ZrP $[\text{Zr}(\text{O}_3\text{P}-\text{OH})_2 \cdot 2\text{H}_2\text{O}]$ have been prepared by interexchange reactions with phenylphosphonic acid where the dihydrogen phosphate group of γ -ZrP is partially replaced by the organic phosphonate.^{11),12)} Some of these have practical applications and are investigated as hosts in intercalation compounds, ion exchangers, photochemical reactions, molecular recognition materials and catalyses, adsorbents for gas separations, and electrochemical devices such as solid state gas sensors.^{3),8),13),14)} In addition, these materials show good thermal stability.⁸⁾ Sulfonated zirconium phenylphosphonate is known as a strong Brønsted acid catalyst (higher than zeolite Y and HZSM-5), an excellent proton conductor³⁾ and a very effective catalyst for a number of organic reactions including the conversion of oximes, semicarbazones and tosylhydrazones to their respective carbonyl compounds.^{15),16)}

Layered titanium (IV) phenylphosphonate $[\text{Ti}^{\text{IV}}(\text{O}_3\text{P}-\text{C}_6\text{H}_5)_2]$ gives the solid with mesoporosity in character and hysteresis.^{5),6),9)} Mesoporosity arises from the adsorption of interparticles and the loss of phenylphosphonate ions due to their hydrozable nature.⁹⁾ Here, we report, for the first time, the synthesis of microporous (without any mesoporosity) layered titaniumphenylphosphonate, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5)_2$ and sulfonated derivative in the presence of sodium dodecylsulfate (SDS) in aqueous media.

2. Experimental

In a typical method, 0.015 mol of TiCl_4 (15 g, 1 M in tol-

uene, Aldrich.) was added to 0.03 mol of phenylphosphonic acid (4.99 g, 95%, Wako Chem.) in 70 g of H_2O under vigorous stirring. 9 mmol of SDS (2.73 g, 95%, Wako Chem.) was then added and stirred for 40 min. Finally, gel was transferred into a Teflon-lined stainless-steel autoclave and heated statically at 423 K for 36 h. The final product was filtered, washed with distilled water, and dried at 393 K for 1 day. Surfactant was removed by stirring the mixture of 1 g of titanium phenylphosphonate with 50 g of dry ethanol and 3 ml of HCl (1 M) at 333 K for 2 h. Finally, the product was filtered, washed with ethanol and dried at 393 K for 1 day and is referred to as Sample 1. For comparison, Samples 2 and 3 were prepared according to the procedure described by Villa-Garcia et al.⁶⁾ In a typical synthesis of sample 2, 3 g of TiCl_4 in 20 g of distilled water was added to 60 ml of a 1 M solution of phenylphosphonic acid while heating at 373 K for 2 h. The resultant solid was also washed with distilled water (until pH=4) and then air dried at 323 K. Sample 3 was prepared by reacting 60 ml of a 1 M solution of phenylphosphonic acid with 25 ml of a solution of TiCl_3 (0.5 M). The reaction mixture was treated at 353 K for 7 days. Finally, the product was filtered, washed and dried at 323 K. Sample 4 was prepared by slow decomposition of a titanium(IV) fluorocomplex in the presence of phenylphosphonic acid, following the procedure described by Dines and Digaicomo.⁵⁾ The phenyl group was readily sulfonated.³⁾ The sulfonation reaction was carried out by adding 3 g of Sample 1 (8.34 mmol) to 17 mmol of fuming sulfuric acid (15.13 g, 20%, Aldrich Chem.). The mixture was kept at 348 K for 1 h. H_2O was added dropwise to convert the excess SO_3 to H_2SO_4 followed by the addition of 100 ml of methanol and then the sample was centrifuged. Elemental analyses of the samples were carried out using ICP (Shimadzu ICPV-1017). Characterization of the samples was obtained using XRD (Cu $K\alpha$ radiation, $\lambda = 0.15406 \text{ nm}$), N_2 adsorption-desorption at 77 K (Bellsorp 28), TG-DTA (Seiko, SSC/5200, heating rate = 5°C min^{-1}), UV-VIS (JASCO V-560) and FT-IR (Perkin Elmer Spectrum One) using a KBr pellet.

3. Results and discussion

Elemental analysis of Sample 1 found, 13.34% Ti, 39.96% C, 2.82% H and 17.20% P. These values are consistent with the molecular formula, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5)_2$; 13.30% Ti, 40.01% C, 2.78% H, 17.23% P. The sulfonated Sample 1 gives, 10.31% Ti, 31.06% C, 2.94% H, 13.35% P and 6.14% S, which matches the molecular formula $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.89}(\text{O}_3\text{PC}_6\text{H}_5)_{1.1} \cdot 1.8\text{H}_2\text{O}$; 10.32% Ti, 31.04% C, 2.93% H, 13.37% P, 6.14% S. This result well agrees with TG analysis results as discussed later. In Fig. 1, XRD patterns of Samples 1, 2, 4 and sulfonated Sample 1 are shown. XRD patterns of all the samples are similar^(1,3,4,6) which indicates they are isostructural (have a similar structure) to $\alpha\text{-Zr}(\text{O}_3\text{P}(\text{OH})) \cdot \text{H}_2\text{O}$.⁽²⁾ Sulfonated Sample 1 retained its crystallinity after sulfonation, i.e., intensity of the low angle peak (d_{001}) remained unchanged, whereas broadening of peaks occurred between 25 and 30° in comparison to parent Sample 1 (Figs. 1(a) and (d)). When zirconium phenylphosphonate was subjected to sulfonation, its crystallinity severely decreased.⁽³⁾ It is clearly evident that titanium phenylphosphonate is more resistant to sulfonation in comparison to zirconium phenylphosphonate. Interplanar spacings, d_{001} of Samples 1, 2 and 3 are 1.43, 1.45 and 1.46 nm, respectively, which are smaller than that of zirconium phenylphosphonate ($d_{001} = 1.47 \text{ nm}$)⁽¹⁾ due to having smaller ionic radii of Ti^{4+} {0.075 nm, octahedral (oh)} compared with Zr^{4+} (0.086 nm, oh). However, d_{001} of Sample 1 increased from 1.43 nm to 1.64 nm after sulfonation. Figure 2 shows the N_2 adsorption-desorption isotherms of Sample 1 featuring a type-I isotherm, which is characteristic of microporous material. The pore size distribution curve calculated from the adsorption branch of the isotherm using

Fig. 1. XRD profiles of Sample 1 (a), Sample 2 (b), Sample 4 (c) and sulfonated Sample 1 (d).

Fig. 2. N_2 adsorption-desorption isotherms of Sample 1 (Inset: Pore size distribution curve).

Barrett-Joyner-Halenda (BJH) exhibits the absence of mesoporosity in Sample 1 (Fig. 2; inset).⁽¹⁷⁾ N_2 adsorption-desorption isotherms of Samples 2, 3 and 4 are type IV with hysteresis loop, an indication of mesoporous materials.⁽⁶⁾ Samples 2, 3 and 4 contain a very small amount of microporosity as there is very small adsorption at $p/p \leq 0.05$.⁽⁶⁾ The pore size distributions of the adsorption branches of Samples 2, 3 and 4 exhibit broad pore size distributions with peak pore diameters (pore size maxima in pore size distribution curve) at 12, 13.6 and 70 nm, respectively.⁽⁶⁾ The porosity characteristic for all the samples are presented in Table 1. Surface area of Sample 1 is $264 \text{ m}^2 \text{ g}^{-1}$. Surface area of Samples 2, 3 and 4 are 143, 61 and $79 \text{ m}^2 \text{ g}^{-1}$, respectively.⁽⁶⁾ Surface area of Sample 1 is 2- to 4-fold those of Samples 2, 3 and 4.

FT-IR spectra of Samples 1, 2 and sulfonated Sample 1 are shown in Fig. 3. Spectra of Samples 1 (after SDS removal) and 2 are similar (Figs. 3(a) and (b)). Sample 1 before SDS removal shows intense CH bands at 2850 and 2945 cm^{-1} , which are absent in Sample 1, confirming the complete removal of surfactant after ethanol-acid treatment (Fig. 3(a)). H_2O and OH groups in Samples 1 and 2 are negligible, as a very weak band exists at approximately 3400 cm^{-1} . The phenyl $\nu(\text{C}=\text{C})$ bands appeared at 1438, and 693 and 749 (out of plane), and 728, and the typical bands for these materials at $3056 [\nu(\text{C}-\text{H}) \text{ aromatic}]$, 1157, 1085 and $1013 \text{ cm}^{-1} [\nu(\text{P}-\text{O})]$ are present.^(3,7) No band exists at approximately 924 cm^{-1} , indicating the absence of P-OH groups in Samples 1 and 2.⁽⁷⁾ The sulfonated product yielded several new peaks. Free -OH groups appeared at 3855 and 3747 cm^{-1} . The broad band in the hydroxyl region (3436 cm^{-1}) results from the presence of both SO-H and H_2O stretching vibrations. Many other new peaks appeared at 1226 cm^{-1} (S-O). In addition, the phenyl ring out-of-plane bands at 693 and 804 cm^{-1} indicate that the ring is now meta disubstituted.⁽³⁾

TG analyses of Sample 1 before and after SDS removal, Sample 4 and sulfonated Sample 1 are shown in Fig. 4. Samples 1 (before and after SDS removal) and 4 show less than 1.3% weight loss below 433 K, indicating the absence of H_2O . Small weight loss (below 1.3%) is due to physically absorbed H_2O (Figs. 4(a), (b) and (c)). Sulfonated Sample 1 lost 7% (or 1.80 moles) of H_2O , resulting from the loss of interlayer H_2O below 433 K. Sample 1 before surfactant removal shows three distinct points of weight loss at 473, 550 and 693 K ; the first two slopes are due to decomposition and desorption of SDS (7.7%), respectively, and the latter (last) one is due to the loss of phenyl groups. Samples 1 (after SDS removal) and 4 show one distinct period of weight loss which starts at 693 K and is completed at 800 K , being equal to 33.8%, which is almost equal to the content of the phenyl group. Sulfonated Sample 1 shows four plateaus: one begins at 340 K (water), the second and third weight loss periods begin at 400 and 560 K to represent a split of either SO_2 or SO_3 and the fourth one represents the burning of

Table 1. Porosity of Titanium (IV) Phenylphosphonates

Sample	$S_{\text{BET}} / \text{m}^2 \text{ g}^{-1}$	Peak pore diameter / nm	Porosity	Reference
Sample 1	264	n.a. ^a	micropore	This work
Sample 2	143	12	mesopore	6
Sample 3	61	13.6	mesopore	6
Sample 4	79	70	mesopore	6

^an.a. = not applicable.

Fig. 3

Fig. 4

Fig. 5

Fig. 3. FT-IR spectra of Sample 1 (a), Sample 2 (b) and sulfonated Sample 1 (c).

Fig. 4. TG analyses of Samples 1, before (a) and after surfactant removal (b), Sample 4 (c) and sulfonated Sample 1 (d).

Fig. 5. UV-VIS spectra of Sample 1 (a) and Sample 2 (b).

phenyl groups. The total weight loss observed for Samples 1 (before SDS removal), 1 (after SDS removal), 4 and sulfonated 1 are 41.6, 34.4, 35.2 and 48.5%, respectively, whereas the expected values are 41.3, 33.6, 33.6 and 48.7%, respectively. In Fig. 5, UV-VIS spectra of Samples 1 and 2 are shown. The presence of a band at approximately 300 nm confirms the octahedral coordination of titanium in titanium phenylphosphonate.

The micropore of Sample 1 results from interlayer space. It may be possible that SDS creates micropore voids in the layers by a growth blocking mechanism, i.e., the layers have to grow around SDS molecules, whereas in Samples 2, 3 and 4, mesopores most likely originate due to two reasons; the end-side particle interactions, some of which could be internal pores formed by cutting layers owing to hydrolysis, and the loss of phosphonate ions because of their more hydrolysable nature.⁹⁾ Ti^{4+} ions covalently bonded to six oxygens of six different phenylphosphonate groups. The phosphonate group is a tetrahedral coordinated to three oxygens and one phenyl group, therefore the phosphorous ion has a positive charge, which may hydrolyze in acidic solution. When sodium dodecylsulfate (SDS) was used, the negatively charged dodecylsulfate ions stabilize the positively charged phosphorous (P^{5+}) cations. It may also be possible that SDS acts as surfactant. SDS is known as a structure-directing agent (surfactant) like hexadecyltrimethylammonium bromide in the formation of the micelle and interacts with inorganic species to form uniform mesoporous inorganic materials.¹⁸⁾ Microporous layered titanium phenylphosphonate may exist within the mesopore, because after the calcinations at 873 K the obtained amorphous material is mesoporous in character. Microporous titanium phenylphosphonate may be useful as shape- and size-selective molecular sieving applications. Sulphonated microporous $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5\text{SO}_3\text{H})_{0.89}(\text{O}_3\text{PC}_6\text{H}_5)_{1.1} \cdot 1.8\text{H}_2\text{O}$ would be a very effective catalyst as it has strong Brønsted acidity (greater than that of ZeY and ZSM-5),¹⁶⁾ it is a proton conductor²⁾ and it is shape-selective for a number of organic reactions including the conversion of oximes, semicarbazones and tosylhydrazones to their respective carbonyl compounds, like sulfonated zirconium phenylphosphonate.^{15),16)}

In conclusion, for the first time, microporous titanium phenylphosphonate, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5)_2$ and sulfonated derivative, $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.89}(\text{O}_3\text{PC}_6\text{H}_5)_{1.1} \cdot 1.8\text{H}_2\text{O}$ were pre-

pared in the presence of sodium dodecylsulfate. The surface area of titanium phenylphosphonate is $264 \text{ m}^2 \text{ g}^{-1}$.

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