Comprehensive Studies on Phosphoric Acid Treatment of Porous Titania toward Titanium Phosphate and Pyrophosphate Monoliths with Pore Hierarchy and Nanostructured Pore Surface

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ARTICLE

Comprehensive Studies on Phosphoric Acid Treatment of Porous Titania toward Titanium Phosphate and Pyrophosphate Monoliths with Pore Hierarchy and Nanostructured Pore Surface

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Simple post-treatments of the porous titania monolith in varied concentrations of phosphoric acid solution provide a series of monolithic titanium phosphates (TiPs) with a hierarchically porous structure together with exquisite macropore surface. Depending on the reaction condition, platy crystallites composed of either $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$, $Ti(HPO_4)_2{\cdot}H_2O$ (α-TiP), or $Ti_2O(PO_4)_2{\cdot}2H_2O$ (π-TiP) are generated on the macropore skeleton via the dissolution and reprecipitation process, which forms distinct wrinkled surface morphologies. In addition, the treatments effectively suppress the shrinkage during drying, leading to the lower bulk density. The post-calcination in air yields porous titanium pyrophosphates preserving the intricate porous architecture in some cases. Notably, the hierarchically porous TiP_2O_7 monoliths prepared from the α-TiP precursors have a good thermal robustness related to the bulk density.

Introduction

A large variety of porous materials are widely used in multifold fields, where each porous morphology and pore size over multiple length scales functions in a specific manner.[1-6] Hence, tailoring an appropriate pore structure depending on each intended use is of importance to enhance the material performance. In addition, the deliberate design of hierarchically porous structure endows an individual porous material with multifunctionality in some cases.[7] On the basis of this background, recent research efforts in material science and industry are intensified toward the architectural design of hierarchically porous materials having more intricate morphology.[8-10]

Up to now, various methodologies to tailor a pore hierarchy have been developed. Among them, liquid-phase processes including the sol–gel technique are undoubtedly versatile and powerful means for this sake.[8-10] Combination of several synthesis ways that provide porous structure in different dimensions gives rise to hierarchically porous geometries. The soft-template method using surfactant micelles is renowned for ordered mesoporous materials,[3,11,12] while the hard-templating of colloidal silica yields the inverse opal structure in the nanometer and micrometer ranges.[13] Meanwhile, the sol–gel processing accompanied by spinodal decomposition offers macroporous co-continuous structure with a narrow pore size distribution and allows the independent control of pore size and volume.[14] Previous studies unveil that hierarchically porous materials with ordered mesopores and well-defined macropores can be obtained by combining the soft-templating and either of the hard-templating or the phase-separation method.[10,13] Most notably, the fine control over the bimodal porosity has been reported in the amorphous silica[10,15] and phenolic resin systems.[16-20]

By contrast, the formation of ordered mesoporosity by the soft-template strategy does not hold good for most of the crystalline materials because the crystal growth readily disturbs the nanometer-scale regular pores formed via the self-assembly of surfactant molecules. Instead, the aggregation of nanometer-sized crystallites affords interstitial voids, which are distinguished as a mesoporous structure. Previously, we reported that well-defined mesopores with no periodicity yet narrow pore size distribution were embedded in the macropore skeleton in the macroporous titania (TiO_2) monoliths obtained by the phase-separation method, resulting in the hierarchically porous material.[21,22]

Despite the difficulty of establishing ordered mesopores by the soft-template method, crystalline materials are still fascinating from the aspect of morphological design, because a variety of unique crystalline shapes reflecting their crystallographic symmetry can be utilized as a building block to introduce more elaborate architecture into the porous solids synthesized by the abovementioned techniques.[23-26] Furthermore, post treatments of the hierarchically porous materials to deliberately set off crystal growth impart an additional texture together with the original porous structure. For example, the flower-like morphology can be constructed on the co-continuous macropore skeleton of the porous titania monoliths by

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Electronic Supplementary Information (ESI) available: [SEM images, N_2 adsorption-desorption isotherms, FT-IR spectra, XRD patterns, flexural stress-strain curves, and summary of pore characteristics of the porous phosphate and pyrophosphate monoliths prepared with different conditions]. See DOI: 10.1039/x0xx00000x harvesting platy crystallites of the layered titanate through the treatment in LiOH aq.[27] In addition, the subsequent calcination converts the whole monolith into the spinel lithium titanate ($Li_4Ti_5O_{12}$) inheriting the intricate morphology, which delivers good performance as an anode for Li-ion and Na-ion batteries.[28]

Very recently, we have reported that the reaction between anatase particles and phosphoric acid (H_3PO_4) yields various titanium phosphate (TiP) crystallites with diverse crystal shape depending on the reaction conditions.[29] This finding suggests the possibility to incorporate an additional texture into the hierarchically porous titania monoliths as is the case with the treatment in LiOH aq. Moreover, the variety of TiP crystals with different shapes may expand the potential of material design in terms of crystal phase and porous morphology, which leads to high-performance TiP materials applicable to electrodes,[29] ion exchangers[30,31] and catalysts.[32,33] The monolithic shape also offers the continuous-flow media for those applications.[34]

In this study, the porous titania monoliths treated in H_3PO_4 aq. under different conditions were comprehensively investigated. The chemical properties as well as the pore characteristics of the products in each condition were explored in detail. We also demonstrate the conversion of the phosphated materials into the pyrophosphate monoliths with hierarchically porous structures. In addition, the difference in thermal durability in terms of the pore properties is discussed.

Experimental

Chemicals

Titanium (IV) *n*-propoxide ($Ti(OPr)_4$), polyethylene glycol (PEG, M_v = 10 000) and phosphoric acid (H_3PO_4, ≥85 wt% in H_2O) were purchased from Sigma-Aldrich Co. Ethyl acetylacetonate (EtAcAc) and 1-propanol (PrOH) were purchased from Tokyo Chemical Industry Co., Ltd. Ammonium nitrate (NH_4NO_3) was obtained from Kishida Chemical Co., Ltd. All reagents were used as received. Distilled water was used in all experiments.

Preparation of titania monoliths

Porous titania monoliths were synthesized by the sol–gel method reported previously.[21] In a typical synthesis, 10 mL of $Ti(OPr)_4$, 7.0 mL of PrOH, 5.0 mL of EtAcAc and 0.9 g of PEG were mixed in a glass tube followed by stirring at 60 °C. After PEG was completely dissolved, the solution was cooled to 40 °C and 2.0 mL of 1 M NH_4NO_3 aq. was added slowly with vigorous stirring. After mixing for 3 min, the obtained homogeneous solution was kept at 40 °C for gelation followed by aging at the same temperature for 24 h. The as-gelled samples were sequentially immersed in ethanol (EtOH), EtOH/H_2O = 1/1 and H_2O at 60 °C for 24 h in sequence to obtain wet titania monoliths.

Treatment of porous titania monoliths in H_3PO_4 aq.

A piece of the wet titania gel was immersed in 20 mL of H_3PO_4 aq. with varied concentrations at different temperatures. The molar ratio of P/Ti in the reaction was >10 in the case of 1 M H_3PO_4 aq. The immersion time was 24 h unless otherwise stated. When the treating temperature was more than 80 °C, the reaction was performed in an autoclave. The resultant samples were subsequently washed with EtOH at 60 °C for 12 h for 3 times followed by drying at 50 °C. Some samples were calcined at different temperatures for 2 h with a heating rate of 5 °C min^{-1}.

Characterization

Microscopic observation was carried out using a scanning electron microscope (SEM; JSM-6060S, JEOL Ltd.), a field emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL Ltd.) and a transmission electron microscope (TEM; JEM-1400 Plus, JEOL Ltd.). Crystal structures were determined by powder X-ray diffraction (XRD; RINT Ultima III, Rigaku Corp.) using Cu Kα (λ = 0.154 nm) as an incident beam. FT-IR spectra were recorded on an FT-IR spectrometer (IR Affinity-1, Shimadzu Corp.) using ground samples that were mixed with KBr to give a 1 wt% sample. N_2 adsorption-desorption measurement was performed at 77 K with BELSORP-mini II (Bel Japan Inc.). The samples were degassed at 120 °C under vacuum before the measurement. Bulk densities were calculated as [weight]/[bulk volume]. Mechanical characteristics of the plate-shaped specimens were measured by a material tester (EZGraph, Shimadzu Corp.) under a quasi-static condition at a crosshead speed of 0.5 mm min^{-1}.

Results and discussion

Formation of Various Nanotextures on Macropore Skeleton of the Porous Titania Monolith

Figure 1 illustrates the morphological change of the porous titania monolith by soaking in 1 M H_3PO_4 aq. at 60 °C for 24 h. As exhibited in the magnified images, the macropore surface became covered with thin wrinkled plates of about several hundreds of nanometers in size after the H_3PO_4 treatment, while both of crack-free monolithic form and macroporous structure remained intact. Effects of the H_3PO_4 treatment conditions (concentration and temperature) on the formation of wrinkled structure were investigated in detail as described hereinafter.

The SEM images of the porous titania treated in varied concentrations of H_3PO_4 aq. at 60 °C for 24 h are presented in Figure 2 (a). It was found that the treatment in the relatively low concentration of 0.1 M H_3PO_4 aq. allows the morphological change of the macropore surface. Although the size and population of generated wrinkles were small when the H_3PO_4 concentration was low, the prolonged reaction time provided more developed wrinkled structure, as shown in Figure S1. The rise in treatment temperature also resulted in more distinct surface asperity (Figure S2). It is noteworthy that the shape of the objects formed on the macropore surface became platy when the temperature was elevated to 100–120 °C. On the other hand, no morphological change was observed when the porous titania was treated in 0.1 M H_3PO_4 aq. at 150 °C and 180 °C. Comparing the SEM images in

Figure 2 (a), the increment of the H_3PO_4 concentration has small influence on the surface morphology between 0.5 M and 3 M. In the case of 4 M H_3PO_4 aq., however, the disk-shaped crystallites were formed on the macropore surface. Further increase of the concentration to 5 M enabled the quicker change of surface morphology yet bought severe damage to the co-continuous macroporous structure. The variation of porous morphology demonstrated in Figure 3 indicates the formation of wrinkled texture on the macropore surface within 4 h followed by the dissolution of the original macropore skeleton, ending up with the thorough collapse of the whole porous geometry as well as the monolithic shape after 24 h.

The change in surface morphology described above is reminiscent of that by the flower-like surface modification of porous titania in LiOH aq. reported previously.[27] It is put forward that titania is somewhat dissolved in LiOH aq. followed by the crystallization and precipitation of layered lithium titanate species onto the titania surface, resulting in a flower-like texture. The wrinkled surface morphology observed in this study is deduced to be formed by a similar mechanism of dissolution of reprecipitation.[35] The collapse of the porous structure in 5 M H_3PO_4 aq. is derived from too strong dissolution tendency of titania relative to the reprecipitation rate.

For the purpose of characterizing the products that constitute the surface texture, FT-IR and XRD measurements were carried out for the samples reacted in H_3PO_4 aq. under different conditions. Comparing the FT-IR spectra of the samples before and after the treatment (Figure 2 (b)), the broad band centered at 1000 cm^{-1}, which is attributed to the P–O stretching vibration, is detected in the samples treated in H_3PO_4 aq.[36] As the H_3PO_4 concentration increases, the intensity of this band becomes stronger and the bands assigned to the O–P–O bending modes appear at 400–730 cm^{-1}.[36] The XRD patterns in Figure 2 (c) confirm the formation of $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ in the samples treated in 0.5–3 M H_3PO_4 aq. at 60 °C, whose crystal water accounts for the perceivable band at 1625 cm^{-1} attributed to water in the FT-IR spectrum. The persisting XRD peaks of anatase indicate that the innate macropore skeleton remained unchanged while the generated wrinkled objects were composed of $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ crystals. Meanwhile, the sample treated in 4 M H_3PO_4 aq. predominantly consisted of $Ti(HPO_4)_2{\cdot}H_2O$ (α-TiP) according to the corresponding XRD pattern, implying that most of the titania macropore skeleton transformed into α-TiP after the treatment. This is the reason why the crystallites that configurate the surface texture are different in shape between the samples treated in ≤3 M and 4 M H_3PO_4 aq. Nevertheless, both $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ and α-TiP tend to form in a platy crystals via a solution processing as reported in the previous literatures,[29,37] thereby producing flower-like morphologies on the macropore skeletons.

Although the crystal phase of the main macropore skeleton remained anatase after reacting in ≤3 M H_3PO_4 aq. at 60 °C, the constituent titania particle size increased by the treatment, as shown in Figure 4 (a). This is probably due to the crystal growth in the hot water condition. In the case of 4 M H_3PO_4 aq., the crystal transition into α-TiP resulted in the larger crystallites associated with the shape change into elongated particles. Since the porous titania monolith possesses mesopores as interstices of constituent particles, the increase of particle size resulted in the enlargement of intrinsic mesopores as observed in Figure 4 (b). On the other hand, the specific surface area decreased as the crystal growth proceeded in the higher concentration of H_3PO_4 aq. (see Table S1).

As mentioned above, the samples treated in 0.1 M H_3PO_4 aq. at ≥150 °C exhibited no change in macropore surface morphology. The FT-IR spectra of the samples treated in 0.1 M H_3PO_4 aq. at different temperatures (Figure S2 (b)) show the enhancement of band intensity corresponding to the P–O vibration at higher temperature except for the case of 150 °C. It means that the reaction between titania and phosphoric acid is somehow suppressed under this condition. The concentration-temperature region where the flower-like texture can be obtained is also limited within moderate conditions in the titania-LiOH aq. system reported previously.[27] The reason still remains elusive but it is deduced that the high reaction temperature improves the crystallinity of the titania particles, which hinders the dissolution. It is also plausible that the outermost phosphated layer acts as a sort of passivation film in such a low-concentration H_3PO_4 aq. In contrast to the reaction between titania and LiOH aq., when the concentration of H_3PO_4 aq. was increased to higher than 1 M, the intricate morphology was formed on the macropore surface at ≥150 °C, as described later.

The morphological variation of the porous titania with wrinkled surface on heating is demonstrated in Figure S3. Both of surface texture and macroporous structure were retained at 600 °C, whereas the former was lost by the calcination at higher than 800 °C. The XRD patterns of the calcined samples (Figure S4) reveal that the $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ crystal phase turn to amorphous on heating due to the dehydration followed by the crystallization into $(TiO)_2P_2O_7$, which is responsible for the loss of the wrinkled macropore surface. The mesopores in the macropore skeleton were collapsed as well above 800 °C due to sintering, as shown in Figure S5.

Nanostructural Design of Titanium Phosphate and Pyrophosphate Monoliths

As indicated in Figure 3, the treatment of the porous titania in 5 M H_3PO_4 aq. at 60 °C is detrimental to the macroporous structure. Nevertheless, the further study on the reaction of porous titania in H_3PO_4 aq. revealed that highly concentrated solution (≥10 M) allows the surface modification with flower-like structure without significant damage on the macroporous morphology, as presented in Figure 5. As already discussed, the balance between dissolution and reprecipitation rates is a key for texturing flower-like structure on the pore surface. It is therefore speculated that the solubility of titania decreases in ≥10 M H_3PO_4 aq. due to the fairly high concentration of phosphate ions. However, the reaction rate tends to be different between the surface and inside of the titania monolith because it takes longer time to complete the solvent exchange due to the high viscosity of the solution, causing a crack formation. Hence, a thin plate (~5 mm thick) of porous titania monolith was immersed in the highly concentrated solution at room temperature for 12 h to let phosphate ions diffuse throughout the porous monolith, followed by the reaction at 80 °C for 4 h. During the treatment at room temperature, no significant damage on the co-continuous macroporous structure was detected. Note that, even by this procedure, the macroscopic structure was collapsed due to the drastic growth of the crystals when the reaction temperature and/or the holding time were increased too much.

The treatment of porous titania in 10 M and 12 M H_3PO_4 aq. yielded the flower-like morphologies consisting of α-TiP platy crystals analogous to the sample treated in 4 M H_3PO_4 aq. at 60 °C for 24 h, as shown in Figure 5 and S6. By contrast, no distinct surface texture was formed by the reaction in 14.6 M H_3PO_4 aq. and the whole porous monolith was composed of α-TiP crystallites having a similar granular shape. The α-TiP crystals formed on the macropore surface in 12 M and 14.6 M H_3PO_4 aq. are compared in Figure 6. The basal plane area of the platy α-TiP crystal became smaller while the thickness increased, when the concentration of H_3PO_4 aq. was changed from 12 M to 14.6 M. As for the α-TiP crystals inside the macropore skeleton, the increment of the concentration increased particle size due to the enhanced crystal growth, resulting in the enlargement of mesopores (Figure S7).

Figure S8 and S9 show the morphological change on heating for the samples treated in 12 M and 14.6 M H_3PO_4 aq., respectively. In both cases, the crystal phase was transformed into a single phase of TiP_2O_7 after the calacination at ≥800 °C (see Figure S10). In comparison with the samples treated in low-concentration H_3PO_4 aq. (Figure S3), the surface morphology constituted by platy crystals was preserved even after the calcination at 800 °C in the case of 12 M. This distinction is probably traced to the different crystal phases of the platy crystals. It appears that the α-TiP crystals show less change in shape through the crystal phase transition than the $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ platy crystals.[27] The calcination at 1000 °C thoroughly disrupted the flower-like morphology, while the co-continuous macroporous structure as well as the crack-free monolithic shape was maintained. It is noteworthy that ~1 μm TiP_2O_7 grains were aggregated into the macropore skeleton, which is regarded as the hierarchically porous structure. The TiP_2O_7 monoliths with the similar hierarchical porosity can be also obtained from the samples treated in 14.6 M H_3PO_4 aq., as demonstrated in Figure S9. This point is also distinguished from the case of the treatment in a low-concentration solution, where the nonporous feature of the macropore skeleton after heating at 1000 °C because of the high sintering tendency of rutile,[21] as observed in Figure S3.

The treatment of porous titania in highly concentrated H_3PO_4 aq. gives rise to porous monoliths consisting of a single-phase α-TiP (and TiP_2O_7 after calcination), while that in a low-concentration solution provides porous TiO_2 monoliths equipped with $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ platy crystallites, as described above. In this study, we have also explored the synthesis protocols to obtain porous monolithic materials composed of a single phase of other TiPs. The comprehensive study for this sake figured out that porous monoliths constituted either by $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ or $Ti_2O(PO_4)_2{\cdot}2H_2O$ (π-TiP) can be prepared by the hydrothermal reaction as displayed in Figure 7. In both materials, the platy crystallites densely grew up on the macropore skeleton. The former inherited the macroporous structure, whereas the large sheet-like crystallites occupied the original pores and the co-continuous structure was hardly recognized in the latter. Because of the thorough crystal transformation from anatase in the whole monoliths, the constituents of the macropore skeleton were also changed into nanosized platy crystallites. It should be noted that the monolithic form was not compromised by the hydrothermal treatment in spite of the drastic change of microscopic morphology.

Figure S11 shows the XRD patterns of the samples calcined at different temperatures, which confirms that the calcination at ≥800 °C allows the crystal transition into a single-phase $(TiO)_2P_2O_7$. Unfortunately, the microscopic observation of the calcined samples in Figure S12 and S13 disclosed that the multilevel porous geometry was significantly sacrificed in association with the remarkable densification by the calcination at ≥800 °C in both cases. As pointed out previously, the $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ platy crystals readily lose their original morphology during the crystal transition into $(TiO)_2P_2O_7$ and so does the π-TiP nanoplates.

Change in Pore Properties of the Phosphated Specimens on Calcination

The variations of bulk density and specific surface area on calcination for the representative specimens are compared in Figure 8. Focusing on the pore properties of the as-dried samples, the bulk density tends to decrease by the H_3PO_4 treatment due to the reduced shrinkage during drying, while the specific surface area becomes lower owing to the crystal growth. The pore characteristics of the phosphated samples are compiled in Table S1.

The titania monolith without H_3PO_4 treatment substantially shrinked (the linear shrinkage of >20%) at 600 °C compared to the phosphated samples, resulting in the highest bulk density and the lowest specific surface area. On the contrary, no obvious change in bulk density was observed for the phosphated samples in calcining at 600 °C. The reason for the slight decrease of bulk density lies in the relatively large weight loss derived from the dehydration of the hydrated TiP crystals as well as the less shrinkage during the heat-treatment, which is consistent with the limited change in the macroporous morphology and the volume of interparticle spaces (mesopores). Although the decrease in specific surface area by calcination is more prominent because of the crystal growth, the phosphated samples show higher specific surface areas. It is revealed that even the moderate H_3PO_4 treatment (*e.g.* 1 M H_3PO_4 at 60 °C) of the porous titania has a positive influence on the thermal stability regarding the retention of pore properties. It is therefore speculated that the phosphated outermost surface of the crystallites that constitute the macropore skeleton reduces the sintering tendency, resulting in the suppressed shrinkage upon heating.

It is worthwhile noting that the porous α-TiP monoliths (the samples treated in 12 M and 14.6 M H_3PO_4 aq.) exhibited fairly good robustness against heating in terms of the bulk density in stark contrast to the $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ and $Ti_2O(PO_4)_2{\cdot}2H_2O$ (π-TiP) materials, which resulted in the dense monoliths above 800 °C. These results correspond to the change in microscopic structure for each sample during calcination shown in Figure S8, S9, S12 and S13. It seems that the difference in thermal stability is attributed to not only the different crystal transition behaviors upon heating but also the different porous morphologies of the as-dried specimens.

It should be pointed out that although the two α-TiP monoliths produced the similar TiP_2O_7 monoliths by calcining at 1000 °C with respect to the hierarchically porous morphology (Figure S8 and S9) and the bulk density (Figure 8 (a)), they showed remarkable difference in mechanical strength as indicated in Figure S14. It was found that the sample treated in 14.6 M H_3PO_4 aq. ended up with the stiffer TiP_2O_7 monoliths compared to that treated in 12 M H_3PO_4 aq. The higher mechanical strength is presumably due to the smaller crystal grain size, which offers the superior degree of fusion between TiP_2O_7 grains in the macropore skeletons.[38]

Conclusions

The simple post-treatment of the hierarchically porous titania monolith in H_3PO_4 aq. allowed the formation of a variety of intricate nanotextures composed of platy TiP crystallites on the inherited co-continuous macropore skeleton via the dissolution and reprecipitation. When the reaction condition was moderate (for example, the reaction in 1 M H_3PO_4 aq. at 60 °C), the treatment gave rise to the wrinkled macropore surface, which was preserved after heating at 600 °C. As the reaction in a high concentration of H_3PO_4 aq. compromised the macroporous structure of the titania monolith, the short-period treatment yielded the porous α-TiP monoliths with the nanotextured macropore surface, which were converted to the hierarchically porous TiP_2O_7 monoliths. The other TiP monoliths composed either of $Ti_2O_3(H_2PO_4)_2{\cdot}2H_2O$ or π-TiP can also be obtained by the hydrothermal treatments, though the co-continuous geometry was somewhat disturbed owing to the crystal growth. The calcination of the two TiP monoliths produced the $(TiO)_2P_2O_7$ monoliths without any crack formation yet accompanied by the significant shrinkage, resulting in the relatively dense materials. However, except for these hydrothermal systems, the H_3PO_4 treatment exhibited the favorable effects on the suppressed shrinkage during drying and calcination, thereby providing the hierarchically porous materials with the lower bulk density than the original porous titania monolith.

Conflicts of interest

There are no conflicts to declare.

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Reaction of porous titania monoliths in H_3PO_4 aq. provides hierarchically porous titanium phosphates with a variety of nanotextured surfaces.