Syntheses of zirconium-containing titania particles with spherical morphology and uniform size by microfluidic reactions

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Monodispersed spherical particles of zirconium-containing titania-octadecylamine with the size of 300–400 nm and CV value of around 5% were synthesized by a sol-gel reaction in the microreactor. Octadecylamine played a roll as a porogen as well as morphological template of spherical particles. The incorporation of zirconium was confirmed by SEM, TG-DTA, XRD and XRF. The hybrids were converted to nanoporous particles without morphological alteration which had the specific surface area of 300 m²·g⁻¹ after removing the porogen (octadecylamine) and that of 60 m²·g⁻¹ after subsequent heat treatment at 600°C, while non-porous products formed by calcination at 600°C without washing with hydrochloric acid/ethanol mixture to remove octadecylamine.

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1. Introduction

Chemical reactions in microreactors have attracted much attention to realize uniform reactions which directly correlate with the homogeneity of products.1,2 In fact, microfluidic reactions have been successfully utilized to synthesize a variety of inorganic nanoparticles.3–6 We have reported the microfluidic syntheses of spherical particles of silica-hexadecyltrimethylammonium and titania-octadecylamine hybrids, which were used as precursors of nanoporous materials.7–9 The reactions are based on the nucleation in the microreactor and subsequent particle growth in an open vessel. Taking advantage of the two step reactions, we obtained titania-octadecylamine hybrid particles with wide size range retaining well-defined particle shape and size as well as homogeneity of the composition.9

Here, we report the co-precipitation of zirconium with the titania-octadecylamine hybrid spherical particles to demonstrate a merit of microfluidic syntheses for the preparation of homogeneous products with the complex composition. The spherical particles of nanoporous titania, which we have successfully synthesized, possess homogeneity of the composition and particle size, therefore, the functionalization and applications of them are worth investigating. It is known that the heteroelement doping resulted in the products with modified properties of titania.10–12 In the present study, zirconium-containing titania was prepared by the microreactor as an example of heteroelement doped titania. Zirconium-containing titania has already been prepared as catalysts for dehydrogenation, decomposition of chlorofluoro carbons, partial oxidation as well as photocatalysts.13 Zirconium-containing titania particles with well-defined shape, size and nanostructure will lead modified performance in catalysts applications.

2. Experimental section

2.1 Materials

Titanium tetra-isopropoxide (abbreviated as TTIP) was purchased from Tokyo Chemical Industry Co., Ltd. Zirconium tetra-n-butoxide (85–90%, diluted with 1-butanol; abbreviated as ZTB) and iso-propyl alcohol (abbreviated as IPA) were purchased from Kanto Chemical Co., Ltd. Octadecylamine (abbreviated as ODA) was purchased from Sigma-Aldrich, Inc. All the reagents were used without further purification.

2.2 Sample preparation

The microreactor synthesis is schematically illustrated in Fig. 1. A microreactor which had Y type junction and cross section of ca. 1 mm² (YMC, Inc.) was used in the present study (shown in Fig. 1 inset). The partial hydrolysis of TTIP and ZTB were occurred in the micro-channel and then the reaction solution

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containing pre-formed nuclei was poured into another solution for particle growth. TTIP/ZTB/IPA mixed solution (Solution A) and IPA aqueous solution (Solution B) were flowed at 20 mL min⁻¹ using a syringe pump (YMC, Inc.) and were mixed within the Y type junction micro-channel that was made of PTFE. Total volume of Solution A, B each was 12.5 mL and the molar ratio of TTIP:ZTB:12 HO in the solution A and B was 1:0.02, 0.1. Then, the mixture of the solution A and B was poured into ODA/IPA aqueous solution (Solution C) under magnetic stirring. Total amount of IPA and 12 HO in the starting solutions was 87.3 and 0.377 mL, respectively. The amount of each component in the starting solutions is shown in Table 1.

<table>
<thead>
<tr>
<th>Solution A</th>
<th>Solution B</th>
<th>Solution C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP (ml)</td>
<td>ZTB (g)</td>
<td>IPA (ml)</td>
</tr>
<tr>
<td>0.458</td>
<td>0.0142</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0707</td>
</tr>
</tbody>
</table>

Table 1. Amount of each component in the starting solutions

After the aging at r. t. for 24 h, the products were collected by vacuum filtration with a membrane filter (cellulose acetate, pore size: 0.2 μm), washing with IPA, and then dried at 60°C in air for a day. In order to remove ODA, 150 mg of as-synthesized products were washed with 12 M hydrochloric acid (abbreviated as HCl)/ethanol (abbreviated as EtOH) mixture (0.125/25 = v/v) for 1 h under magnetic stirring and were collected by vacuum filtration with a membrane filter (cellulose acetate, pore size: 0.2 μm). This cycle was repeated twice to remove ODA. Finally, the HCl/EtOH washed products were calcined in air at 600°C for 1 h at a heating rate of 150°C h⁻¹. As a control, as-synthesized products were also calcined under the same condition. Titania co-precipitated with zirconium are denoted as TiZrX (X represents molar ratio of ZTB/TTIP in the Solution A, i.e. 0.02, 0.1) and a non-doped product is denoted as Ti1.

2.3 Characterization

Particle size distributions were obtained by a dynamic light scattering (DLS) technique using Horiba LB-550. In situ observations of nucleation and growth processes were carried out by correcting a portion of reaction solution and adding into excess amount of IPA (200 mL) to eliminate further reaction during DLS measurements. ZrO₂/TiO₂ ratio of each product was estimated by X-ray fluorescence (XRF) analyses using Rigaku ZSX Primus II. Scanning electron micrographs (SEM) were obtained on a Hitachi S-2380N scanning electron microscope. Prior to the measurements, the samples were coated with 30 nm gold layer. Average particle size and coefficient of variation (CV) value were obtained by each SEM image for counting 100 particles. Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Rigaku TG-8120 instrument at a heating rate of 10°C min⁻¹ under air flow and using α-alumina as a standard material. X-ray diffraction (XRD) patterns of products were recorded on a Rigaku RAD IIB powder diffractometer equipped with monochromatic CuKα radiation operated at 20 mA and 40 kV. The size of crystallites was calculated using the Scherrer’s equation based on the full width at half maxima of anatase (101) reflection at 2θ = 25.176° and the rutile (110) reflection at 2θ = 27.358°. Nitrogen absorption/desorption isotherms of the HCl/EtOH washed and calcined products were measured at −196°C on a Belsorp Mini instrument (Bel Japan, Inc.). Prior to the measurements, the samples were dried at 140°C under nitrogen atmosphere for 3 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method by using a linear plot over the range of P/P₀ = 0.05–0.20. Pore size distributions of the HCl/EtOH washed and calcined products were derived from the nitrogen adsorption isotherms by the Barrett–Joyner–Halenda (BJH) method. Porosity volume was determined from the amount of nitrogen adsorbed at P/P₀ = 0.90. Based on the hypothesis of which the sample is composed of one cylinder, this technique is applied to obtain pore volume of nanoporous solids. In the present case, P/P₀ = 0.90 is not the last point of each adsorption isotherm. We chose the point to estimate pore volume because some rise, which was attributed to nitrogen adsorption onto external surface, was seen on each adsorption isotherm.

3. Results and discussion

When the IPA solution of TTIP and ZTB was mixed with aqueous IPA in the microreactor, a homogeneous transparent solution was obtained. The solution was subsequently mixed with IPA aqueous solution containing ODA (Solution C) and the solution became turbid after ca. 30 s, indicating the particle growth. This reflects that the present syntheses are composed of the formation of nuclei in the first step (mixing Solution A with B) and their growth in the second step (mixing with Solution C). We performed DLS measurements to experimentally confirm nucleation and growth processes of titania particles. As shown in Fig. 2, uniform-sized particles with the size of several nanometers which are thought of as titania nuclei are seen, and they became larger when the nuclei were added into Solution C. Similar phenomena may occur in the solutions containing TTIP and ZTB. Primarily formed zirconium-containing titania nuclei grew under the presence of ODA in the second step. Pinnavai et al. reported the syntheses of nanoporous silica by a neutral templating method and they also proposed a possible formation mechanism where silicon alkoxides and alkylamine formed rod-like micelles by hydrogen bonding in an ethanol aqueous

![Fig. 2. Particle size distributions of titania particles just after mixing Solution A with Solution B within the microreactor for nucleation (dashed line) and just after mixing that solution with Solution C for particle growth (solid line).](image-url)
solution. After that, Antonelli and Gedanken et al. extended the method to the syntheses of nanoporous titania particles. The template amine molecules were removed by treating as-synthesized products with acidic ethanol because of weak bonding between titania framework and alkylamine. In the present case, the mechanism is also applied to explain the formation of zirconium-containing titania-ODA hybrid particles and subsequent nanostructure formation by solvent extraction. White precipitate formed at the bottom of a reaction vessel and the solution was slightly turbid after aging for 24 h. A solid product was separated by filtration and the weights of the filtrate suggested the product yields of ca. 90% (as calculated by taking into account that the weight loss of 45 wt% for Ti1Zr0.02 and 40 wt% for Ti1Zr0.1 in the TG curves in the temperature range of 25–600°C, which was ascribed to the desorption of adsorbed water and thermal decomposition of ODA), indicating almost all of the TTIP and ZTB were precipitated. The composition of the products was determined by XRF analyses. The molar ZrO2/ TiO2 ratios of Ti1Zr0.02 and Ti1Zr0.1 were 0.021 and 0.095 respectively, which coincided with the values in the corresponding starting solutions. SEM observations of the as-synthesized products are shown in Fig. 3. Well-defined spherical particles were observed in the SEM and the monodispersity was supported by the particle size distributions (Fig. 4) which were derived from the SEM images. CV values, which represent monodispersity of particle size, of Ti1, Ti1Zr0.02 and Ti1Zr0.1 were 7.9, 5.4 and 5.4%, respectively. Based on the earlier studies on monodispersed colloids, these values are small enough to mention that they are monodispersed. Rengarajan et al. pointed out that CV value lower than 6% was necessary to form an opal-like ordered structure, photonic crystal, by simulation and experiments. Our zirconium-containing titania samples satisfy that condition, therefore it seems possible to fabricate photonic crystals, although other study showed CV value around 3% was desired to form such ordered structure. The average particle sizes of Ti1, Ti1Zr0.02 and Ti1Zr0.1 were 453, 477 and 462 nm, respectively (the size is consistent with our previous communication of titania-ODA hybrid spherical particles). The average particle sizes were almost the same irrespective of the presence of zirconium. Since it is possible to synthesize titania-ODA hybrid spherical particles with the size range of several tens of nm to microns, the incorporation of zirconium into hybrid particles with different size seems to be possible.

ODA was removed by washing with HCl/ EtOH to give porous products as reported for the titania-ODA hybrid spherical particles. The nitrogen adsorption/desorption isotherms of the washed products and BJH pore size distributions derived from corresponding isotherms are shown in Fig. 5 to show the porosity of the washed products. Ti1 had BET specific surface area of ca. 450 m²g⁻¹ and BJH pore size was around 2 nm, while BET specific surface area was 300 m²g⁻¹ for Ti1Zr0.02 and Ti1Zr0.1, and BJH pore size was smaller than 2 nm as shown in Fig. 5(B). The TG-DTA curves of HCl/EtOH washed products are shown in Fig. 6. Two exothermic reactions were seen for Ti1Zr0.02 and Ti1Zr0.1, while one exothermic reaction was
observed for Ti1. The exothermic reaction at around 250°C, which accompanied weight loss of 7–8%, was due to the thermal decomposition of ODA. These residual ODA may be concerned for the smaller BET specific surface areas of the zirconium-containing products. In order to remove ODA completely, washing conditions should be optimized and will have larger BET specific surface area, possibly equal to that of Ti1.

The exothermic reaction at 368°C was attributed to the phase transition of the amorphous titania into anatase, since no weight change was observed in the corresponding TG curve (Ti1). For zirconium-containing products, the reaction appeared at higher temperature region (421 and 487°C for Ti1Zr0.02 and Ti1Zr0.1). Okada et al. investigated the phase transition of titania-silica and titania-germanium oxide hybrid by DTA and showed amorphous to crystal phase transition at around 400°C for titania occurred at higher temperature region as the amount of dopants increased. Judging from these results, zirconium was incorporated into titania framework and played a role in retarding the phase transition of amorphous titania.

XRD patterns of calcined zirconium-containing titania were attributed to anatase (JCPDS 21-1272). Ti1 was transformed into anatase with the size of 25 nm and contained small fraction of rutile (JCPDS 21-1276) with the size of 32 nm after the heat-treatment at 600°C as shown in the XRD pattern (a). The size of anatase and rutile crystallites in each product is summarized in Table 2. Only anatase of 18 nm for Ti1Zr0.02 and 21 nm for Ti1Zr0.1 in size formed in zirconium-containing products and the crystallites were relatively small compared with those in Ti1 because of the retardation of anatase to rutile transformation as reported by many researchers regarding the effect of doping on the crystal phase transition of titania (that phenomena were well summarized in Hanaor’s review45).

In Fig. 8, nitrogen adsorption/desorption isotherms of titania and zirconium-containing titania after removing ODA and calcination at 600°C for 1 h and BJH pore size distributions derived from corresponding isotherms are shown. BET specific surface area of titania was ca. 30 m²·g⁻¹, while Ti1Zr0.02 and Ti1Zr0.1 had that of ca. 60 m²·g⁻¹. In addition, Ti1Zr0.1 showed

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**Fig. 5.** Nitrogen adsorption/desorption isotherms (A) and BJH pore size distribution (B) of products with different molar zirconia/titania ratio after removing ODA. (a) ⊗ Ti1, (b) □ Ti1Zr0.02, (c) ⊘ Ti1Zr0.1. Open symbols and closed symbols represent adsorption and desorption isotherm, respectively.

**Fig. 6.** TG (A) and DTA (B) curves of products with different molar zirconia/titania ratio after removing ODA, (a): Ti1, (b): Ti1Zr0.02, (c): Ti1Zr0.1.
Fig. 7. XRD patterns of products with different molar zirconia/titania ratio after removing ODA and calcination at 600°C, (a): Ti1, (b): Ti1Zr0.02, (c): Ti1Zr0.1.

Table 2. Particle size, CV value, BET surface area, pore volume and crystallite size of products with different molar zirconia/titania ratio. A and R represent anatase and rutile, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Size (nm)</th>
<th>CV (%)</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Crystallite size (nm)</th>
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</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>as-synthesized</td>
<td>453</td>
<td>7.9</td>
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<td>—</td>
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<td></td>
<td>ODA removal</td>
<td>435</td>
<td>8.7</td>
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<td></td>
<td>ODA removal, 600°C 1 h</td>
<td>346</td>
<td>8.4</td>
<td>28</td>
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<tr>
<td>Ti1Zr0.02</td>
<td>as-synthesized</td>
<td>477</td>
<td>5.4</td>
<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>ODA removal</td>
<td>364</td>
<td>4.6</td>
<td>329</td>
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<td>ODA removal, 600°C 1 h</td>
<td>326</td>
<td>4.9</td>
<td>52</td>
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<tr>
<td>Ti1Zr0.1</td>
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<td>5.4</td>
<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>ODA removal</td>
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<td>5.2</td>
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<td>0.15</td>
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<td>ODA removal, 600°C 1 h</td>
<td>330</td>
<td>4.7</td>
<td>56</td>
<td>0.10</td>
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</table>

Fig. 8. Nitrogen adsorption/desorption isotherms (A) and BJH pore size distribution (B) of products with different molar zirconia/titania ratio after removing ODA and calcination at 600°C. (a): Ti1, (b): Ti1Zr0.02, (c): Ti1Zr0.1. Open symbols and closed symbols represent adsorption and desorption isotherm, respectively.

4. Conclusions

Zirconium-containing titania-octadecylamine hybrid spherical particles with uniform size of ca. 450 nm, CV value of ca. 5% and molar zirconia/titania ratio of 0.02–0.1 were synthesized by a sol–gel reaction of titanium tetra-iso-propoxide and zirconium a narrower pore size distribution where its peak was centered at 4–5 nm and ranging from 2 to 8 nm compared to those of Ti1 and Ti1Zr0.02 where their BJH pore size distributions were relatively broad, which ranged from 2 to 11 nm. In the case of products directly calcined without HCl/EtOH treatment, it was shown that they were non-porous because of the volume shrinkage during calcination caused by thermal decomposition of ODA which was an intense exothermic reaction. Consequently, we prepared zirconium-containing titania spherical particles. The non-porous product was obtained when the as-prepared ODA-containing product was calcined, while porous one was prepared by removing ODA before the calcination. Depending on the porosity (as well as host–guest reactions using the pore surface), one can expect unique catalytic abilities as well as the modified optical properties. Therefore, further studies on the catalytic and photonic crystal applications are worth conducting. In addition, the success in the microreactor syntheses of zirconium-containing titania motivates us to investigate hybrid particles with various chemical compositions.
tetra-$n$-butoxide in the presence of octadecylamine from a homogeneous iso-propyl alcohol aqueous solution by means of the microreactor. The as-synthesized zirconium-containing titania particles were converted to nanoporous spherical particles whose BET specific surface area were ca. 300 m$^2$·g$^{-1}$ before and 60 m$^2$·g$^{-1}$ after anatase formation, while nanoporous titania had that of 450 m$^2$·g$^{-1}$ and 30 m$^2$·g$^{-1}$, respectively. Non-porous zirconium-containing titania particles also formed when the as-synthesized zirconium-containing products were calcined without removing octadecylamine. Zirconium incorporation was suggested by SEM, TG-DTA, XRD and XRF. Microfluidic reactions were successfully applied to the syntheses of particles with homogeneous compositions as well as well-defined morphology, size and size distribution.

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References
29) K. Shiba, K. Onaka and M. Ogawa, manuscript in preparation.