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1. Introduction

An increasing number of environmental measures are being implemented to achieve Sustainable Development Goals. In the chemical and ceramic industries, waste reduction, recycling and reuse of materials, increasing the energy efficiency, and so on have attracted attention. From this viewpoint, it is necessary to revise the materials used and their manufacturing processes.

Zirconia (ZrO$_2$) is one of the most important ceramic materials in modern society. It has good mechanical strength, chemical stabilities and functionalities such as ionic conductivity, and optical properties. It has wide applications, such as catalysts and its support, gas sensors, and dental implants. Various types of ZrO$_2$ and its derivatives are used for a wide variety of requirements. Particularly, composites of ZrO$_2$ nanoparticles and polymers have been developed to improve their mechanical and optical properties.

The properties of ZrO$_2$ depend on its crystal structure. There are three polymorphs, monoclinic(m-), tetragonal(t-) and cubic(c-) ZrO$_2$, at ambient pressure. The room temperature phase is m-ZrO$_2$. It undergoes phase transitions to t-ZrO$_2$ and c-ZrO$_2$ at 1200 and 2400 °C, respectively. These high-temperature phases can be stabilized at room temperature by using various methods. For example, solid solutions of ZrO$_2$ and additives such as Y$_2$O$_3$ and CaO have cubic and tetragonal phases, which are known as stabilized ZrO$_2$. A crystallite size is also an important factor for the stabilization of the high-temperature phase. Nanocrystalline ZrO$_2$ often contains meta-stable t-ZrO$_2$. This method takes advantage of the property of supercritical water. When water reaches its critical point of 374 °C and 22.1 MPa, the properties of density, ionic product, and dielectric constant decrease significantly. This result causes rapidly a supersaturated condition for many inorganic substances. While water can dissolve many substances under hydrothermal and sub-critical conditions, supercritical water scarcely dissolves inorganic substance. Such a significant change leads to rapid homogeneous nucleation to yield nanoparticles.

The nanoparticles of ZrO$_2$ are also synthesized by using the supercritical hydrothermal method. They often contain m-ZrO$_2$ and metastable t-ZrO$_2$. The phase compositions depend on the synthesis conditions such as temperature, reaction time, starting materials, and additives. In general, short supercritical hydrothermal treatments tend to lead to the formation of metastable phases. Co-existing substances, such as KOH and alcohol, also affect the phase compositions.

In addition, these studies used various kinds of zirconium salts as starting materials, which lead to byproducts...
The samples were washed by using ion-exchanged water, and wastewater containing counter anions. These damage the apparatus in subcritical and supercritical conditions. In the present study, we used zirconium basic carbonate, which is a mild acid salt that is insoluble in water under ambient conditions, as a starting material. It dissolves in water under sub-critical conditions, and then, it transforms nanosized zirconia at the critical point. Our nano-sized zirconia also contained both m- and t-ZrO₂, which is considered to be stabilized by the coexistence carbonate ions. Thanks to the feature that byproducts are only water and carbon dioxide, the process developed here allows environmental-friendly synthesis ZrO₂ nanomaterials without involving the wastewater treatment.

2. Experimental procedures

Zirconia nanoparticles were synthesized by using the supercritical hydrothermal method. Figure 1 shows a schematic of the batch-type supercritical hydrothermal apparatus. The volume of the reactor vessel was 50 cm³, and it was made of hastelloy C 276. The temperature in the vessel was recorded using a thermocouple. A safety line that maintained the pressure below 30 MPa was connected at the upper side of the vessel to the backpressure valve. A sintered ceramic filter with 0.5 μm pores was set between the vessel and the back pressure valve to protect them.

Commercially available zirconium basic carbonate (Jiangxi Kingan Hi-tech Co., Ltd., China) was used as a starting material. This material and ion-exchanged water were mixed to form a slurry composed of 50 wt% zirconium basic carbonate and 50 wt% water. The slurry was stirred continuously by using a magnetic stirrer. The amount of slurry introduced into the vessel was 17 ml.

Supercritical hydrothermal treatments were performed at 400 °C and 30 MPa. The temperature in the reactor vessel was increased after 50 min. Then, the condition was maintained for 0, 1, and 10 h. After the treatments, the reaction vessel was placed in water to quench the samples. The samples were washed by using ion-exchanged water, filtrated, and dried at 60 °C in a vacuum oven overnight.

Powder X-ray diffraction (XRD) patterns of the samples were measured with MiniFlex 600C (Rigaku corporation, Japan), which is equipped with a high-speed one-dimensional detector D/teX Ultra 2 (Rigaku corporation, Japan). Cu-Kα radiation and Ni-Kβ filter were used for the measurements. A divergence slit was set at 1.25°. The XRD patterns were analyzed by using the fundamental parameter method with SmartLab Studio II software (Rigaku corporation, Japan). The ratio of t-ZrO₂ to m-ZrO₂ (t/m ratio) in the samples was estimated by using the reference intensity ratio method with ICDD PDF No. 01-079-1766 and 01-073-8590 for t- and m-ZrO₂, respectively.

The particle size and morphology of the obtained samples were investigated via transmission electron microscope (TEM) observations using JEM-2000FX (JEOL Ltd., Japan). The powder samples were dispersed in ethanol and then dropped on Cu grids with a carbon film. The particle size distributions of each sample were collected by 100 particles randomly-selected from several TEM images of each sample. The specific surface areas of the samples were also analysed by using the volumetric gas adsorption technique performed with BELSORP-mini II (Microtrack BEL Corp., Japan). The samples were preheated at 150 °C under a vacuum condition. N₂ adsorption–desorption isotherms at 77 K were analyzed by using the Brunauer–Emmet–Teller (BET) method.

Fourier transform infrared spectroscopy (FT-IR) were performed in the transmission mode using FT/IR-4600 (JASCO Corporation, Japan). The powder sample was diluted with KBr and measured.

Thermogravimetric and differential thermal analyses (TG–DTA) were carried out using DTG-60H (Shimadzu corporation, Japan). The powder samples were placed in an alumina cell, and the heating rate was set to 10 °C/min.

3. Results and discussion

Figure 2 shows the XRD patterns of the samples prepared under the supercritical hydrothermal treatment for different reaction times. The samples had different patterns, which indicated that the obtained samples continued to change during the supercritical treatments. The observed peaks can be assigned to t- and m-ZrO₂. The lattice parameters and ratio of t-ZrO₂ to m-ZrO₂ (t/m ratio) are summarized in Table 1. The lattice parameters of t-ZrO₂ were changed during the supercritical hydrothermal treatments, while those of m-ZrO₂ reasonably agreed with the literature data. The t/m ratio was also reduced, i.e., phase transition from t-ZrO₂ to m-ZrO₂ occurred. Thermal treatments at 400 °C in air do not cause phase transition. (See Fig. S1 in the supplemental material.) Since supercritical water has a low solubility for inorganic substances, these changes were not caused by the dissolution–precipitation process. However, the phase transition from t-ZrO₂ to m-ZrO₂ is active in water, and it is considered that water molecules have a significant impact on the crystal structure of ZrO₂. Thus, this phenomenon is also true in supercritical water.

The profiles of the XRD patterns were rather broad. Table 2 lists the crystallite sizes of the samples. The long supercritical treatments tended to sharpen the peaks of...
both \( t\)-ZrO\(_2\) and \( m\)-ZrO\(_2\). These results indicated enlargement of the crystallites and/or improvement of the crystallinity. The TEM observations were performed to measure the particle size as shown in Fig. 3. Each sample contained particles with the diameter of approximately 20 nm, but the diameter distribution range differed. The sample synthesized in supercritical water for 0 h shows the narrow particle size distribution of 10–20 nm. The average diameter was 14 nm. However, long supercritical hydrothermal treatments induced another peak at 17 nm in the distribution, and the original peak around 14 nm decreased. Coarse particles larger than 20 nm were also observed. The average diameter increased with the supercritical hydrothermal treatments. The trends of these sizes were similar tendency to the crystallite size trends estimated by XRD and the surface area \( S_{\text{BET}}\) of the sample, as shown in Table 2. These results indicate that our nanoparticles have the same properties as the ZrO\(_2\) nanoparticles synthesized supercritically hydrothermally from other zirconium salts, in terms of crystallinity and particle size.\(^{23,24}\) The crystallite size and \( D_{\text{TEM}}\) of each sample are well matched, suggesting that the nanoparticles are single crystals. Moreover, they imply that zirconium basic carbonate dissolved in water as the temperature of the slurry increased. It is difficult to explain these results by crystal growth as supercritical water has a considerably low ion solubility.

According to the literature, zirconia particles synthesized from zirconium salts often adsorb anions derived from the starting material.\(^{23,33}\) To confirm the surface state of ZrO\(_2\) particles, FT-IR was measured as shown in Fig. 4. Several varying absorption bands were identified between 1050–1700 cm\(^{-1}\), which did not originate from the lattice vibrations of \( t\)-ZrO\(_2\) and \( m\)-ZrO\(_2\) crystals.\(^{34-38}\) According to the literatures, these peaks were derived from the adsorbed water and carbon dioxide (CO\(_2\)).\(^{39,40}\) Long-term treatments in supercritical water reduced the peaks around 1050 and 1540 cm\(^{-1}\) marked by dotted lines in the figure, which were attributed to adsorbed CO\(_2\).

To investigate the adsorbed CO\(_2\) on the samples quantitatively, TG–DTA were measured as shown in Fig. 5. Each sample lost about 5 wt\% in weight, which corresponded to the adsorbed water. Additional exothermic peaks around 400 °C were observed in the DTA curves of the samples of 0 and 1 h. According to the literature, zirconia particles synthesized from zirconium salts often adsorbed anions derived from starting materials.\(^{23,33}\) In our study, the additional peaks were considered as the desorption of CO\(_2\). As discussed above, our samples had high crystallinity and the carbonate ions (CO\(_3^{2-}\)) were scarcely incorporated into the ZrO\(_2\) crystals due to their size. Therefore, the desorption CO\(_2\) derived from ones adsorbed on the surface of the particles.

Using the results obtained above, we discussed the reaction mechanism from zirconium basic carbonates to zirconia nanoparticles. Figure 6 shows the schematic of the process. Zirconium basic carbonates are insoluble in water under ambient conditions and form slurry with

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**Table 1.** Lattice parameters and phase compositions of samples

| Samples | Lattice constants \( t\)-ZrO\(_2\) | \( m\)-ZrO\(_2\) | \( t\-m\) ratio / wt % |
|---------|-------------------------------|-----------------|---------------------|
|         | \( a/\text{Å}\) \( c/\text{Å}\) | \( h/\text{Å}\) \( c/\text{Å}\) | \( \beta/\text{°}\) |
| 0 h     | 3.609(9) 5.177(3) 5.146(3) 5.212(4) 5.310(5) | 100% 99.20(3) 51.8(2) |
| 1 h     | 3.591(3) 5.194(3) 5.150(4) 5.216(3) 5.318(3) | 100% 99.23(3) 21.3(2) |
| 10 h    | 3.591(3) 5.263(8) 5.149(11) 5.207(11) 5.311(11) | 100% 99.16(10) 7.17(16) |
| Ref.    | 3.596\(^a\) 5.185\(^a\) 5.146\(^b\) 5.212\(^b\) 5.313\(^b\) | 100% 99.22\(^b\) |

\(^a\)Reference 41).  
\(^b\)Reference 42).
water. They were dissolved in water in a closed vessel as the temperature increased. When the water reached the critical point, zirconia nanoparticles rapidly formed from the solution since the solubility of the inorganic substance was much lower in supercritical water than in subcritical water. While $m$-ZrO$_2$ is the thermodynamically stable phase under the supercritical condition of water, CO$_3^{2-}$ originated from the starting material were adsorbed on the surface of the zirconia nanoparticles. Such adsorbed anions stabilized $t$-ZrO$_2$.16) In the supercritical water, CO$_3^{2-}$ adsorbed on the surface of the zirconia nanoparticles was slowly removed. However, the desorption of CO$_2$ did not immediately induce the phase transition did not occur together. Water molecules played an important role in inducing the phase transition from $t$-ZrO$_2$ to $m$-ZrO$_2$, even in supercritical water. After the phase transition, the particles enlarged due to the difference in the volumes of $m$-ZrO$_2$ and $t$-ZrO$_2$.16)

Finally, we discussed the effect of the starting materials. Table 2 also shows characteristics of the zirconia nanoparticles synthesized by the supercritical hydrothermal reaction with varied starting materials. Our zirconia nanoparticles, which were made from zirconium basic carbonate, contains more $t$-ZrO$_2$ than others. This is due to the influence of the adsorbed anions as discussed above. The nanoparticles made from the carbonate and the alkoxide have similar size while Zr(OH)$_4$ gave rather large particles. Since Zr(OH)$_4$ is also interpreted as ZrO$_2$·nH$_2$O, existing Zr-O-Zr networks may affect crystal growth of zirconia. Even when insoluble zirconia basic carbonate was used as starting materials, the resultant zirconia nanoparticles have similar properties to those made from typical starting materials. Therefore, the carbonate-based synthesis method does not produce polluting effluents as the only byproducts are water and CO$_2$. Therefore, it is an industrially green process.

### Table 2. Summary of the characteristics of zirconia nanoparticles synthesized by the supercritical hydrothermal reaction with varied starting materials

| Starting Material | Reaction time$^b$ | Temp. /°C | Pressure /MPa | $t$-$m$ ratio | $t$-ZrO$_2$ | $m$-ZrO$_2$ | $D_{\text{TEM}}$(µm) | $S_{\text{BET}}$/m$^2$ g$^{-1}$ |
|------------------|------------------|------------|---------------|---------------|------------|------------|----------------|------------------|
| Zirconium basic carbonate  | 0 h  | 400 | 30 | 51.8(2)$^c$ | 12.5(7) | 13.8(5) | 15.10(2) | 14.1(2.1) | 67.84 |
|                    | 1 h  | 400 | 30 | 21.3(2)$^c$ | 15.40(2) | 17.43(16) | 18.60(2) | 16.9(3.0) | 45.66 |
|                    | 10 h | 400 | 30 | 7.1(16)$^c$ | 16.3(4) | 18.97(13) | 20.49(17) | 17.7(3.4) | 39.59 |
| Zr(OEt)$_4$  | 10 min | 400 | 38 | 25$^d$ | 18.0 | 16.0 | 15.6 | — | — |
|                | 10 min | 500 | 38 | 9$^d$ | 25.9 | — | 19.4 | — | — |
| Zr(OH)$_4$  | 10 min | 400 | 38 | 6$^d$ | 37.6 | — | 30.2 | — | — |
|                | 10 min | 500 | 38 | 3$^d$ | 39.7 | — | 35.8 | — | — |

$^a$Reference 23).
$^b$Retention time from the point where the reaction temperature is reached.
$^c$Unit [wt%].
$^d$Unit [vol%].

Fig. 3. Typical TEM images and particle diameter distribution of samples. SD is standard deviation.

Fig. 4. FT-IR spectra of samples.
particles ranged from 10–20 nm. The properties of the particles were similar to those obtained by hydrothermal synthesis from different raw materials. Long treatments in supercritical water induce phase transition from \( t \)-ZrO\(_2\) to \( m \)-ZrO\(_2\). The particle sizes were expanded as long supercritical hydrothermal treatments. This is volume expansion of phase transition triggered by the desorption of CO\(_2\) from the surface. Furthermore, by using basic carbonate as the starting material, the washing process of the products is omitted. This approach contributes to the reduction of wastewater, which is one of the environmental problems.

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![Fig. 5. TG–DTA of samples. Red and black lines represent TG and DTA, respectively.](image)

![Fig. 6. Schematic of the reaction mechanism of nano-zirconia formation.](image)
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