Solvothermal crystallization of nanocrystals of metal oxides

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Abstract. Solvothermal crystallization of the hydroxide gels obtained by hydrolysis of alkoxides (Zr, Ta, Nb, In, Sn, Ti and Al) was examined. Nanocrystals having high surface areas ($S_{\text{BET}} > 170 \, \text{m}^2\,\text{g}^{-1}$) were obtained except for the product derived from indium isopropoxide. The effect of water in organic solvent upon the crystallinity of the product was investigated. The increase in the activity of water by using high concentration of alkoxide or intentional addition of water to the solvothermal medium led to crystal growth of the products. In contrast, decrease in activity of water by adding ethylene glycol before solvothermal treatment caused a decrease in crystallinity of the product.

1. Introduction

Nanocrystalline metal oxides have been widely used as gas sensors [1–3], catalysts [4,5], and electrodes [6–8], because of their unique physical and chemical properties. Therefore, many investigations on the synthesis of nanocrystalline metal oxides have been carried out [9–11]. The sol-gel method is widely applied to synthesize nanomaterials [12,13]. However, the products obtained by this method are usually amorphous, and therefore heat treatment of the products is required to obtain crystalline materials. Heat treatment may cause sintering and loss of the surface area of the products, which may restrict their practical use.

Solvothermal methods are widely explored for the synthesis of nanocrystalline materials [14–16]. In 1989, one of the present authors showed that α-alumina was synthesized from microcrystalline gibbsite (Al(OH)$_3$) in 1,4-butanediol at 285 °C [17], much lower temperature than that required by the hydrothermal reaction. He also examined the reaction of gibbsite in a series of alcohols and found that two different reactions took place depending on the carbon number of the alcohol [18]. When higher alcohols were used as the reaction media, hydrothermal reaction by the water formed by thermal dehydration of the starting material took place [16]. Supposing an amount of water is formed in organic media, the activity of water increases with the decrease in affinity of the media to water. The increase in activity of water leads to adsorption of water on the solid starting particles whereby facilitating the hydrothermal conversion of the starting materials [16]. These arguments imply that even though reaction was carried out in organic solvents, especially inert organic solvents such as toluene and mineral oil, the real chemistry might be hydrothermal one.

In the present research, we synthesized metal (Zr, Ta, Nb, Sn, Ti, In and Al) oxides by solvothermal
crystallization of the hydroxide gels derived by hydrolysis of metal alkoxides. One of the objectives of this work is to examine the effects of the activity of water on the solvothermal crystallization and it was confirmed that water present in the solvothermal reaction affects the crystallinity of the products, crystallite size of metal oxide nanocrystals being controlled by activity of water. Another objective is to synthesize large surface area oxide materials suitable for the catalysts.

2. Experimental

Eight alkoxides were used as precursors: zirconium n-propoxide (ZNP), zirconium isopropoxide (ZIP; Mitsuwa Chemicals Co., Ltd.), titanium tetraisopropoxide, aluminium trisopropoxide (Nakalai Tesque, Inc.), tantalum ethoxide, niobium ethoxide, tin isopropoxide and indium isopropoxide (High Purity Chemicals Co.). A desired amount of an alkoxide was dissolved in 100 mL of toluene. Hydrolysis of the alkoxide solution was carried out by keeping the solution in a constant humidity box (RH = 76 %). Water dissolved from the gas phase into the toluene solution slowly hydrolyzes the alkoxide yielding hydroxide gel. The solution was kept standing until no further change was observed. The thus-obtained hydroxide gel in toluene was transferred into a test tube and it was set in a 300 mL autoclave. An additional 50 mL of toluene was added to the gap between the test tube and the autoclave wall. The autoclave was purged with nitrogen, heated to 300 °C at a rate of 2.5 °C/min, and held at that temperature for 2 h under the autogenous pressure of toluene. The resulting precipitate was washed with methanol and air-dried. Calcination of the product was conducted in a box furnace at desired temperature for 1 h.

Table 1. Physical properties of the products obtained by solvothermal crystallization of the alkoxide-derived hydroxide gel.

| Alkoxide       | Concentration of alkoxide (g (L-tol.)⁻¹) | Calcination temperature (°C) | EG/In ratio | BET surface area (m² g⁻¹) | Crystallite size (nm) | Calculated surface area a (m² g⁻¹) |
|----------------|-----------------------------------------|-------------------------------|-------------|--------------------------|-----------------------|----------------------------------|
| Zr(OC₃H₇)₄     | 15                                      | -                             | -           | 340                      | ND b                  | -                                |
|                | 15                                      | 400                           | -           | 190                      | 5                     | 205                              |
|                | 32                                      | -                             | -           | 370                      | ND b                  | -                                |
|                | 62                                      | -                             | -           | 302                      | ND b                  | -                                |
|                | 103                                     | -                             | -           | 228                      | 4.9                   | 209                              |
|                | 125                                     | -                             | -           | 246                      | 4.7                   | 218                              |
| Ta(OC₂H₅)₅     | 52                                      | -                             | -           | 279                      | ND b                  | -                                |
|                | 52                                      | 700                           | -           | 37.8                     | 19                    | 38                               |
| Nb(OC₃H₅)₃     | 32                                      | -                             | -           | 246                      | ND b                  | -                                |
|                | 32                                      | 700                           | -           | 26.5                     | 76                    | 16                               |
| In(O⁻⁻C₃H₇)₃   | 20                                      | -                             | 8           | 19.5                     | 73                    | 12                               |
|                | 20                                      | -                             | 16          | 38.0                     | 54                    | 16                               |
| Sn(O⁻⁻C₃H₇)₄   | 60                                      | -                             | 8           | 15.6                     | 33                    | 26                               |
|                | 60                                      | 400                           | -           | 186                      | ND b                  | -                                |
| Ti(O⁻⁻C₃H₇)₄   | 29                                      | -                             | 16          | 110                      | 4                     | -                                |
|                | 29                                      | 400                           | -           | 179                      | 8                     | 193                              |
| Al(O⁻⁻C₃H₇)₃   | 30                                      | 400                           | -           | 154                      | 9                     | 171                              |

a Calculated from the crystallite size assuming that each crystallite is truly spherical.
b XRD peak was too broad for determination of the crystallite size.
c Product was γ-alumina.
3. Results and discussion

The BET surface areas and crystallite sizes of the products are summarized in table 1 together with the surface areas calculated from the crystallite sizes. Except for the product obtained from indium alkoxide, all the products had large surface areas over 170 m$^2$ g$^{-1}$. The effect of the solvothermal crystallization on the BET surface area of the product is clearly shown by comparison with the sample obtained by direct calcinations of the hydroxide gel. Whereas the sample calcined at 400 °C after the solvothermal treatment had a surface area of 208 m$^2$ g$^{-1}$, the sample without the solvothermal treatment had only 21 m$^2$ g$^{-1}$ after calcinations at 400 °C.

The XRD patterns of the samples synthesized from various concentration of ZNP are shown in figure 1. All the samples exhibited the patterns due to tetragonal ZrO$_2$, and the sample synthesized from lower concentration of ZNP had smaller crystallite size.

![XRD patterns of zirconia obtained by the solvothermal crystallization of the hydroxide gel derived with various concentrations of ZNP in toluene. Concentration of alkoxide (g (L-toluene)$^{-1}$): (a), 15.4; (b), 32.3; (c), 62.0; (d), 102.7; (e), 125.3.](image)

![FT-IR spectra of: (a) and (b), the gels obtained by hydrolysis of ZNP; (c) and (d), ZrO$_2$ samples obtained by solvothermal crystallization of the gels. Concentration of alkoxide (g/L-toluene): (a), 15.2; (b), 1254.2; (c), 15.4; (d), 125.3.](image)

The DTA curves of the hydroxide gels (data not shown) exhibited an exothermic peak at about 450 °C due to the crystallization of the hydroxide gel into tetragonal ZrO$_2$. On the other hand, the products obtained by the solvothermal treatment of the gel showed no peak due to crystallization but a broad peak due to combustion of organic matter remaining on the surface of the products. The presence of organic matter in the solvothermal products is also confirmed by FT-IR spectra (figure 2). The peaks at 3000–2800 cm$^{-1}$ are due to the C–H stretching vibration modes of alkyl moieties originating from the starting alkoxide. It is rather surprising to note that the solvothermal product possessed a larger amount of alkyl moieties than the precursor gel. Presumably, the alkyl groups in the hydroxide gels are easily hydrolyzed and eliminated during the drying stage, while the alkyl moieties remaining on the surface of ZrO$_2$ crystals are more stable because of difficulty in nucleophilic attack of water at zirconium atom for hydrolysis of the Zr–O–R bond.

As shown in figure 1, the increase in the alkoxide concentration increased the crystallite size of ZrO$_2$. Since the increase in the alkoxide concentration possibly causes an increase in the amount of water absorbed into the mixture at the hydrolysis stage and thus increases the amount of the water in the solvothermal system, the concentrations of water in the solvent and in the hydrolyzed gel were measured (figure 3). The increase of ZNP concentration clearly led to the increase in water
concentration. Therefore, it can be assumed that crystallite size of the product obtained by the solvothermal treatment is related to the water concentration in the system at the solvothermal stage.

The effect of water intentionally added to the medium before the solvothermal treatment was examined. The XRD patterns of the products (data not shown) showed that the addition of water increased crystallite size of tetragonal ZrO$_2$. Therefore, the crystallization of the hydroxide gel in the solvothermal treatment takes place with the aid of water dissolved in toluene and generated from the hydroxide gel. To further investigate the behavior of water present in the system at the solvothermal stage, the effect of the amount of the gel charged for the solvothermal treatment was examined. When a half amount of the gel was charged to the autoclave, the crystallite size of ZrO$_2$ prepared was much smaller than that of ZrO$_2$ prepared under the usual condition. This result indicates that the concentration of water present in the reaction medium was largely decreased by vaporization of water to the gas phase.

![Figure 3.](left) Concentration of water in the hydrolyzed gel / toluene mixture.

![Figure 4.](Right) TEM images of ZrO$_2$ obtained from ZNP with/without the intentional addition of water. Concentration of additional water (g/L-toluene): (a), 0; (b), 14.3.

Figure 4 shows the TEM images of the products obtained from ZNP with and without intentional addition of water at the solvothermal crystallization stage. Well-dispersed nanocrystals of ZrO$_2$ were observed. The average particle sizes of ZrO$_2$ nanocrystals are about 5 and 7 nm for the products obtained without and with the addition of water, respectively. The observed particle sizes are in good agreement with the crystallite sizes (5 and 6 nm, respectively) calculated from the XRD pattern using the Scherrer equation, indicating that each primary particle is a single crystal of zirconia. Surface areas, calculated from crystallite sizes assuming that the primary particle is truly spherical, accord with the BET surface areas (table 1), confirming little aggregation of primary particles took place during the crystallization stage, as is observed in figure 4.

As shown in table 1, the present products had relatively high surface areas and the surface area is easily controlled by the activity of water. However, In$_2$O$_3$ derived from indium isopropoxide had a small BET surface area (19.5 m$^2$ g$^{-1}$) and a large crystallite size (73 nm). The TEM images of this product (data not shown) showed that the In$_2$O$_3$ particle is nearly spherical. The particle size observed from TEM distributed relatively widely ranging from 17 nm to 94 nm, which was much larger than the particle size of ZrO$_2$ obtained from ZNP. The crystallite size (73 nm) calculated from the XRD peak was in this range, suggesting that each particle observed by TEM is a single crystal. In comparison with ZrO$_2$, the difference between BET surface area (19.5 m$^2$ g$^{-1}$) and surface area calculated from the crystallite size (11.5 m$^2$ g$^{-1}$) was large. This is because the In$_2$O$_3$ particles were not completely spherical. The product synthesized at low temperature (150 °C) have broad XRD pattern, but its surface area was very small (35.3 m$^2$ g$^{-1}$). This result indicates that in the case of indium, aggregation of the hydroxide gel occurred before crystallization of In$_2$O$_3$. 

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**Figure 3.** (left) Concentration of water in the hydrolyzed gel / toluene mixture.

**Figure 4.** (Right) TEM images of ZrO$_2$ obtained from ZNP with/without the intentional addition of water. Concentration of additional water (g/L-toluene): (a), 0; (b), 14.3.
To investigate the pore structure, N$_2$ adsorption isotherm was measured (data not shown). The shape of the isotherm of ZrO$_2$ corresponded to type II of IUPAC notation, which indicates that ZrO$_2$ sample had essentially no micropores nor mesopores. The $t$-plot derived from the isotherms exhibited a straight line going through the origin, suggesting the absence of micropores in the product, which indicates that the product particles are well dispersed and free from aggregation.

To synthesize smaller In$_2$O$_3$ particle, an attempt was made to decrease the activity of water, which greatly affects the crystallization behavior under the solvothermal conditions. To suppress the activity of water, ethylene glycol (EG), which has a high affinity to water, was added before solvothermal treatment. Regardless of the EG / In ratio, the XRD pattern is attributed to cubic In$_2$O$_3$, but the increase in the EG / In ratio made XRD peaks broader and crystallite size of In$_2$O$_3$ smaller. Therefore, the crystallite size of In$_2$O$_3$ could be controlled from 73 nm to 33 nm by the addition of EG (table 1).

To demonstrate the effect of the activity of water, the following experiments were also carried out. After hydrolyzing ZNP in toluene, the mixture was centrifuged discarding the supernatant, and the hydroxide gel was dispersed in a fresh portion of toluene, dodecane and ethylene glycol. The XRD patterns of the products showed that the product obtained in dodecane having a lower affinity to water than toluene, had larger crystallite size than that obtained in toluene, while ethylene glycol gave much smaller crystallite size. These results clearly confirm that the activity of water has an importance role on crystallization process, and that the activity of water can be controlled by selection of the solvothermal medium.

4. Conclusions
The nanocrystals of metal oxides having large surface areas and small crystallite sizes are synthesized by slow hydrolysis of metal alkoxide followed by solvothermal crystallization in organic solvents. In solvothermal reaction, the crystallinity of metal oxide nanocrystals is greatly affected by water dissolved in the solvent. It was confirmed that the change in the activity of water by the intentional addition of water or ethylene glycol is effective to control the crystallite size of metal alkoxide.

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**Supplementary Data**

**Figure S1.** Raman spectra of zirconia obtained by the solvothermal crystallization of the hydroxide gel derived from ZNP: (a) as-synthesized; (b) calcined in air at 400 °C
Supplementary Data

Figure S2. XRD patterns of ZrO$_2$ obtained by solvothermal crystallization of the hydroxide gel: (a) under the usual condition; (b) by lowering the charged amount of the gel to the autoclave. (a), 12.5 g of ZNP in 100 mL of toluene, and (b) 6.3 g of ZNP in 50 mL toluene was treated in a 300 mL autoclave following the ordinary hydrolysis stage.
**Supplementary Data**

**Figure S3.** XRD patterns of ZrO\(_2\) obtained from ZNP and ZIP.