Emanation Thermal Analysis (ETA) of Sol–Gel Derived Mesoporous Titania

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Mesoporous titania has been prepared by the sol–gel method with surfactant templating. The wet gels, obtained by hydrolysis of Ti-alkoxide in alcoholic solutions with acid catalyst, were immersed in surfactant solutions, dried and annealed. The annealed gels were labeled with $^{228}$Th and $^{228}$Ra, and the release rate of $^{228}$Rn, produced by alpha-decay, was measured during heating and cooling to obtain the ETA–curves. The gels were also characterized with TGA–DTA, XRD, nitrogen adsorption, SEM and AFM. The pore size and the microstructure of the gels obviously depended on the size and shape of the surfactant micelles. The ETA results clearly showed the differences in the surface area and the thermal stability of the annealed gels. The evaluated ETA results and the structural changes of the gels during heating were discussed.

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1. Introduction

Recently, interests in titania are growing because of its potential applications such as photocatalyst,\textsuperscript{3}\hspace{1em} photoelectrode,\textsuperscript{4}\hspace{1em} gas sensor,\textsuperscript{5}\hspace{1em} etc. For many applications, titania with mesopores and large surface area are suitable. Various methods have been proposed for the preparation of porous titania, e.g. sol–gel method\textsuperscript{3–6}\hspace{1em} and direct deposition from aqueous solutions.\textsuperscript{7}\hspace{1em} The effects of the surfactant or polymer templating on the microstructure of mesoporous titania have been reported previously.\textsuperscript{5,6}\hspace{1em} Structural analysis is also important to develop new methods for preparation of mesoporous ceramics. The porous structure of solid is usually characterized by gas-adsorption. In this study, the emanation thermal analysis (ETA) has been made to evaluate the thermal evolution of sol–gel derived titania with surfactant modification. The ETA is based on the release of radioactive gases from solid samples, and is a useful tool to evaluate the thermal evolution of solids with large surface area, e.g. fine powders and gels.\textsuperscript{8–11}\hspace{1em} The numerical analysis of ETA curves for mesoporous titania has been made by the diffusion structural analysis (DSA)\textsuperscript{12}\hspace{1em} and the results are discussed in comparison with other characterization techniques.

2. Experimental procedures

Titania wet gels were prepared by hydrolysis of Ti(O–nC$_4$H$_9$)$_4$ in ethanol solution with addition of ethylacetocetate using acid catalyst.\textsuperscript{5,6}\hspace{1em} After aging at 90°C for 1 h, the wet gels were immersed into an ethanol solution of surfactants, Cetyltrimethylammonium chloride (CTAC) or Benzyltrimethylammonium chloride (BTAC), at 60°C for 1 h, and dried at 90°C for 24 h (surfactant-modified gels). The wet gels were also aged and dried to obtain the xerogels without modification. The dried gels were annealed at 600°C for 2 h.

The changes of the microstructure of the gels by heating were evaluated using thermogravimetric- and differential thermal analysis (TGA–DTA, Rigaku, TAS–100), N$_2$-adsorption (Quantachrome, Autosorb), X-ray diffraction (XRD, Rigaku, RAD–C), and the emanation thermal analysis (ETA). After annealing at 600°C, ETA measurements were made. ETA curves show the $^{228}$Rn–release rate, $E$, of the samples, previously labeled with $^{228}$Th and $^{228}$Ra, during heating.\textsuperscript{8–11}\hspace{1em} Atoms of $^{228}$Rn are formed by α-decay of $^{228}$Th and $^{228}$Ra which are incorporated into the sample due to recoil energy (85 eV/atom) to the maximal depth of 67 nm, as calculated by TRIM code.\textsuperscript{13}\hspace{1em} An increase in the radon release rate, $E$, indicates an opening of the structure and/or an increase of the surface area, whereas a decrease in $E$ reflects a densification of the structure, pore closure and/or a decrease in the surface area of the sample. A more detailed description of the principles, the method, and the apparatus of ETA can be found elsewhere.\textsuperscript{8–11}\hspace{1em} The heating rate was 5 K/min, and the sample weight was 0.1 g. The samples were immersed in a stream of dry air, flowing at a rate of 40 mL/min.

The structural changes by heating were also discussed using TG–DTA and N$_2$ adsorption. The specific surface area, pore size distribution, and pore volume of the gels, before and after annealing, were estimated by the Barret–Joyner–Halenda (BJH) method\textsuperscript{14}\hspace{1em} using N$_2$ adsorption-desorption curves.

3. Results

3.1 XRD, TGA–DTA, N$_2$-adsorption\textsuperscript{11}\hspace{1em} The results of XRD, TGA–DTA and N$_2$-adsorption have been reported in.\textsuperscript{11}\hspace{1em} The diffraction peaks of anatase and the weak peaks of rutile were observed for all of the samples after annealing at 400°C and 600°C, respectively. The microstructural properties are shown in Table 1. After annealing at 600°C, the specific surface area of the surfactant-modified gels was nearly the same as that of the gels without modification, but the pore size distributions are different. The pore size, as well as the pore volume, increased with the modification, and the most probable pore size depended on the surfactant species.

3.2 ETA\hspace{1em} The ETA results are shown in Figs. 1–3. The Rn emanation rate $E$ for all of the annealed gels increased in three temperature ranges, around 200°C, 500°C to 700°C and around 1000°C, and a remarkably decreased around 800°C. The changes in $E$ for the gels without modification are less significant.

4. Discussion

4.1 Microstructure of surfactant-modified gels\hspace{1em} The crystalization behaviors of the gels were hardly affected by surfactant-modification.\textsuperscript{5}\hspace{1em} The effects of surfactant immersion were found only on the porous properties. Pore size increased by surfactant-modification, and depended on the size of surfactant micelles. The pore volume also increased. As previously reported,\textsuperscript{6}\hspace{1em} surfactant micelles were incorporated into the gels, and restrict shrinkage during drying, resulting in
Table 1. Preparation Conditions and Properties of TiO₂ Xerogels, Dried at 90°C for 24 h and Annealed at 600°C for 2 h (selected from Table 1 in[1])

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Surfactant] (mol/l)</th>
<th>t* (h)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>R² (nm)</th>
<th>Rₘax (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xerogel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTAC modified xerogel</td>
<td>0.22</td>
<td>1</td>
<td>32.3</td>
<td>0.093</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>C3</td>
<td>0.22</td>
<td>1</td>
<td>34.6</td>
<td>0.107</td>
<td>5.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

* immersion time
*² Average pore radius
*³ Pore radius at the peak of pore size distribution curves

Fig. 1. ETA results for the annealed titania gel without surfactant modification.

Fig. 2. ETA results for the annealed titania gel with CTAC modification.

Fig. 3. ETA results for the annealed titania gel with BTAC modification.

larger pores after annealing. The pore size depended on the surfactant species, and was about two times of the micelle diameter.¹⁵

4.2 Evaluation of ETA curves

The ETA curves have been evaluated by the method, Diffusion Structural Analysis (DSA), proposed by Beckman and Balek.¹² The Rn-release rate E from porous bodies may be written as

\[ E(T) = E_{Recoll} + E_D(T) \Psi(T) \]  \hspace{1cm} (1)

where \( E_{Recoll} \) is the Rn release by recoil, \( E_D(T) \) is the Rn permeability, and \( \Psi(T) \) is the changes in the microstructure near the solid surface depending on temperature, i.e., changes in surface area, pore size and shape, crystalline phases, etc., by heating. In the mathematical model used in this study,¹² the temperature dependence of the emanation rate due to diffusion was assumed to be expressed by Eq. (2).

\[ E_D(T) = \{ p_1 p_2 \exp(-p_2/T) \} \left[ \coth \left( \frac{3}{p_1} p_3 \exp(-p_2/T) \right) \right] - \{ p_1 \exp(-p_2/T) \} \left/ 3 \right. \]  \hspace{1cm} (2)

where \( p_1, p_2 \) and \( p_3 \) were parameters used for fitting of ex-
Experimental curves. The characteristic values of Rn diffusion, \( D_0 \) and \( Q \), were estimated using the following relations.

\[
D = D_0 \exp\left[-\frac{Q}{RT}\right] \quad (3)
\]

\[
D_0 = (p_1 p_2)^3 L_0^2 \lambda / 9 \quad (4)
\]

and

\[
Q = 2 p_1 p_2 R \quad (5)
\]

where \( L_0, \lambda \) and \( R \) are the average diffusion length of \(^{220}\text{Rn} \) (ca. \( 10^{-4} \text{ cm} \)), the \(^{220}\text{Rn} \) decay constant (0.12 s\(^{-1} \)) and the gas constant, respectively. The structural changes of annealed gels by heating, which affect the emanation rate, were assumed to be expressed with Eq. (6).

\[
\Psi(T) = 1 - \left(\frac{p_1}{2}\right) \left[1 + \text{erf}\left(\frac{(T-p_2)}{(2p_2)\sqrt{1/2}}\right)\right] \quad (6)
\]

The parameters \( p_1, p_2 \) and \( p_6 \) were used for fitting of experimental ETA curves with the model, where \( p_1 \) and \( p_2 \) were the maximum temperature and the temperature interval of the structural changes in the diffusion path by heating (annealing process), e.g. decreases in number and size of open pores by sintering, etc., respectively.

The ETA results show the increases of \( E \) in three temperature ranges, suggesting three different mechanisms for Rn release for different temperature ranges. The fitting curves in the low temperature range, from the room temperature to 350 °C, are shown in Fig. 4. In this temperature region, the structural changes of the annealed gels, deposition of anatase and sintering, may not proceed. Thus, the increase in \( E \) may be attributed to the increase in the effective surface area for Rn release due to desorption of adsorbed gases, mainly H\(_2\)O. The saturation of \( E \) values in the temperature range from 200 to 300°C may support this.

The fitting curves in the temperature range from 400 to 1000 °C are shown in Fig. 5. In the lower temperature range in this region, \( E \) increases with increasing temperatures. The increase in \( E \) may be attributed to the increase in the Rn permeability through open pores and to Rn release during deposition of anatase. In the upper temperature range, the \( E \) values decrease with increasing temperature. The estimated curves of \( \Psi(T) \) are shown in Fig. 6. These curves clearly show the differences in the thermal behaviors of the gels. The annealing process of the xerogel, probably sintering of the gel, begins at the lowest temperature. The annealing process of the BTAC-modified gel takes place in the lower temperature range than the CTAC-modified gel. From these curves, the characteristic temperatures of annealing, \( T_{\text{ana}} \) and \( T_{\text{fml}} \) were obtained, and they are shown in Table 2 with the characteristic values of Rn diffusion, \( D_0 \) and \( Q \). The higher \( T_{\text{ana}} \) for the surfactant-modified gels show that the thermal stability of their microstructure is better than the xerogel without modification. The onset-temperature of the annealing, \( T_{\text{ana}} \) for the BTAC-modified gel is the same as the CTAC-modified gel, but \( T_{\text{fml}} \) is lower. This result clearly shows the difference in the microstructure of these surfactant-modified gels, as well as shown by the smaller pore size and the pore volume estimated from N\(_2\) adsorption curves. The decrease in pore size and surface area of the gels with large pores, estimated by the BJH method, is less than those of the gels of smaller pores in this temperature region. Thermal stability of the porous structure is important for application of gels to heterogeneous catalysts. Differences in \( D_0 \) may suggest the structure of solid phase near the surface, several 10 nm in depth (the penetration depth of \(^{220}\text{Rn} \) by recoil), is affected by surfactant-modification. The larger value of \( D_0 \) for the xerogel suggests the larger number of
open pores. The lower activation energy for the modified gels may be attributed to the larger open pores.

5. Conclusions

Effects of the surfactant-immersion method on the microstructure and thermal stability of the annealed titania gels have been discussed with DSA using ETA results.

1. Changes in the microstructure of porous materials during heating can be evaluated by DSA using ETA results.
2. With surfactant-modification, pore size and shape depend on the size and shape of surfactant micelles. The microstructure of the surfactant-modified gels is thermally stable in comparison with that of the gels without modification.

References