Preparation of Porous Titania by Sol–Gel Method Using Alkylketene Dimers as a Template

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Porous titania (TiO₂) particles were prepared using a sol–gel technique employing Alkylketene Dimers (AKD) as a template. The effects of incremental additions of AKD as a template material on crystal structure, surface and internal morphology, and pore properties were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption/desorption. The prepared titania had more than one pore size on its surface and internally. Incremental addition of AKD caused an increase in specific surface area. The prepared porous titania with the addition of AKD at 5 wt% exhibited a high specific surface area of 124 m²/g, which is markedly higher than in titania without AKD (53.5 m²/g). To quantitatively evaluate the porous structure, we performed fractal analysis over a wide scale using box-counting, small X-ray scattering (SAXS) and the FHH (Frenkel–Halsey–Hill) method. Porous titania showed fractal properties, both on its surface and internally.

Introduction

Solid catalysts are widely used in the chemical industry and are generally composed of the catalytic substances and supports (Catalysis Society of Japan ed., 1985). Catalytic substances have active sites throughout, but catalytic activity can occur only on their surfaces. Consequently, great efforts have been made to maximize the surface area of the catalysts by distributing them over their supports. Numerous researchers have attempted to develop a method of building highly dispersed and stably supported catalysts (Kikuchi et al., 1992; Takahashi, 2004; Basagiannis et al., 1997; Zanella et al., 2004; Basagiannis et al., 2008; Sugawara et al., 2008).

The support materials are also important, since their pore properties significantly influence the performance of the catalyst. This has led to the development of mesoporous supporting materials with high active reaction areas and catalyst loading amounts, as well as monolithic materials with macro pores that govern overall substance transport being prepared (Kresge et al., 1992; Takahashi et al., 2004; Endo et al., 2006; Konishi et al., 2009).

Support materials with a hierarchically several size a pores, such as meso- and macroporosity, are attracting increasing research attention (Takahashi et al., 2004; Yu et al., 2007). Porous materials with several size a pores are prepared by employing dual templates. The control of the porosity is normally achieved by combining suitable templates for the required length scale organization: for example, surfactant micelles are used for directing mesoporosity, and polystyrene latexes for macroporosity (Holland et al., 1998; Zhao et al., 2011). However, this strategy has several drawbacks, such as the need for dual template materials and limitations in the synthesis conditions.

Mayama and Tsujii (2006) reported that porous silica material with Menger sponge-like fractal geometries could be prepared by using only template particles of Alkylketene Dimers (AKD) alone, which spontaneously forms super-water-repellent fractal surfaces. They showed that the morphology of the support materials has a significant influence on the catalytic performances. However, there are no reports on the synthesis of other materials using this technique.

In the present study, we focused on titania as the objective support material, since it has high stability and a strong affinity for active substances. Having synthesized porous titania using AKD as a template, we performed fractal analysis to make a quantitative evaluation of material morphologies.
1. Experimental

1.1 Preparation of AKD particles

Figure 1 shows the structural formula of AKD, particles of which were prepared using the following procedure. Raw AKD (Newpel Hard 76G, NOF Corporation) was dissolved into n-hexane (Special Grade, Wako Pure Chemical Industries, Ltd.) at approx. 13.25 wt%, and then refined by recrystallization at 282 K and solid–liquid separation. The refined AKD was again dissolved into n-hexane at approx. 13.25 wt%. The solvent was then evaporated using a vacuum rotary evaporator at 298 K and $15 \times 10^3$ Pa for 10 min to obtain AKD particles. Finally, the solvent-free AKD particles were heat-treated at 318 K for 60 min. These procedures were conducted in an air atmosphere. AKD particles were grind into a range from several µm to several tens of µm by a mortar and pestle.

1.2 Preparation of titania particles

Titania was prepared using the sol–gel method. To obtain the precursor solution, titanium tetraisopropoxide (TTIP) as the titania source, $\text{H}_2\text{O}$ for hydrolysis of the TTIP, hydrochloric acid (HCl) as the catalyst, and EtOH as the solvent were used. The solution was prepared at a molar ratio of TTIP : $\text{H}_2\text{O}$ : HCl : EtOH = 1 : 20 : 0.17 : 109 (Yusef et al., 2001). AKD particles (0, 1, 3 or 5 wt%) were added to the precursor solution, and the mixture was stirred for 1 h at 313 K, and then for 3–5 d at room temperature. The AKD was then removed by calcination at 773 K for two hours. Titania particles were grind into a range from several µm to several tens of µm by a mortar and pestle.

1.3 Characterization

Crystal structure analysis was performed by X-ray diffraction (XRD, Miniflex, RIGAKU Co., Ltd.). The surface morphology and internal structure of the prepared AKD and titania were observed by scanning electron microscopy (FE-SEM, SU8000, HITACHI Ltd.) and transmission electron microscopy (FE-TEM, JEM-2100, JEOL Ltd.). The porosity characteristics of the prepared titania were determined by $\text{N}_2$ adsorption and desorption (BELLSORP-mini, MicrotracBel Ltd.). The fractal structure of the prepared titania was analyzed by small X-ray scattering (SAXS, NANO-Viewer, RIGAKU Co., Ltd.).

2. Results and Discussion

2.1 Characterizations of porous titania

Figure 2 shows the XRD patterns and the SEM images of the prepared samples; (a) AKD particles, (b) titania precursor samples with AKD at 5 wt% (Uncalcined) and (c) titania particles with 5 wt% AKD.

Figure 2(c) shows post-calcined titania particles with 5 wt% AKD. In the XRD pattern, AKD peaks disappear during calcination, and as result, a single-crystal structure of anatase (JCPDS21-1272) is obtained. The SEM images confirmed that several size pores have been formed on the titania particle surfaces. Figure 3 shows the FE-SEM images of the morphology of the prepared titania influenced by incremental addition of AKD: titania without AKD had a flat surface (Figure 3(a)), while the prepared titania with AKD had a lumpy surface (Figures 3(b)–(d)). The number of macro pores on the titania surface was increased with incremental addition of AKD. These SEM images suggest that the lumpy surface is composed of the submicron- to micron meter-scale pore structures that show fractal-type scale invariance. It might be that the morphology of the AKD is transferred to the titania surface. Figure 4 shows the FE-TEM images of the prepared titania with 0 and 5 wt% AKD, which show that both types consist of the primary nano particles. However, the prepared titania with 5 wt% AKD had several nano pore sizes inside. This internal structure may also show fractal-type self-similarity. Figure 5 shows the $\text{N}_2$ adsorption–desorption isotherm of the prepared titania particles, and the inset shows the pore-size distribution as determined from the desorption branches (DH). Although the prepared titania with 0, 1 and 3 wt% AKD showed a type IV isotherm, indicating that these samples had developed mesopores, the prepared titania with 5 wt% AKD showed a type II isotherm.
Incremental addition of AKD particles caused the specific surface area of the prepared titania to increase. The prepared titania with AKD at 5 wt% had several sizes pores in its surface, and it also exhibited a much higher specific surface area (124 m²/g) than the prepared titania without AKD (53.5 m²/g). The prepared titania with AKD at 5 wt% also had a wider pore-size distribution ($r_p = 7.99$ nm) than the prepared titania without AKD ($r_p = 3.09$ nm). The adsorption performance of the titania particles was controlled by incremental addition of AKD particles.

2.2 Fractal analysis

The surface and internal structure of the prepared titania with AKD at 5 wt% may follow fractal-type self-similarity as observed in the SEM and TEM images. To quantitatively characterize the surface structure, we determined the fractal dimensions of cross sections of the prepared titania particles by the box-counting method using the FE-SEM and TEM trace images. The equations for calculation of the surface
fractal dimension are as follows (Shibuichi et al., 1996; Ono et al., 2009).

\[ N(r) \propto r^{-D_{\text{cross}}} \]  \hspace{1cm} (1)

Where, \( r \) is the size of the boxes, and \( N(r) \) is the number of boxes to cover the object. The surface fractal dimension \( D \) is calculated as in Eq. (2).

\[ D = D_{\text{cross}} + 1 \]  \hspace{1cm} (2)

**Figure 6** shows the log \( N(r) \) against log \( r \) plot for AKD particles and the prepared titania at 5 wt%. Surface fractal dimension \( D \) was determined from the slope of this figure. The surface fractal dimension was rarely differed from AKD particles and porous titania with AKD samples (ca., \( D = 2.1 \)). We conduct that the morphology of AKD was transferred to the surface of the obtained titania. SAXS measurements were performed to determine the internal fractal dimension in the nano-region. **Figure 7** shows the SAXS profiles obtained. Mass fractal dimension \( D_m \) was determined from the slope in this figure.

In the results, the prepared titania with AKD at 5 wt% exhibited a fractal dimension of approximately \( D_m = 2.47 \). To quantitatively measure the internal structure in the sub-nano region, fractal analysis was carried out using the FHH method from \( N_2 \) adsorption measurements data. **Figure 8** shows the fractal dimension \( D_i \) as determined by FHH-plot. The FHH-plot is given by Eqs. (3) and (4) (Meng et al., 1997).

\[ V \propto \left[ 1 / \ln \left( P_i / P \right) \right] [1 / m] \]  \hspace{1cm} (3)

\[ D_i = 3 - 1 / m \]  \hspace{1cm} (4)

Where, \( V \) is the adsorbed quantity, \( 1 / m \) is the slope of the FHH-plot, and \( P/P_0 \) is the relative pressure. The fractal dimension of the internal structure was rarely departed from that of the prepared titania with or without AKD. We attributed this to the fact that both types of titania with a fractal dimension were calculated at the adsorbed site. This technique clearly has limitations under these experimental conditions.

In the present study, we obtained porous materials with several size pores that had fractal properties both on the surface and in their internal structure. This porosity or frac-
tal structures may be of benefit in applications that require adsorption (separation) and catalysis (reaction). The specific surface area was discovered to be proportional to the mass fractal dimensions (shown in Table 1). We will, therefore, further investigate the influence of fractal characteristics on potential for catalytic applications in Process Systems Engineering in the future.

Conclusion

In the present study, porous titania was successfully synthesized employing the sol–gel method and using AKD as a template for various added amounts of AKD. The XRD patterns of prepared titania particles exhibited a single-crystal anatase structure. The prepared titania particles using AKD as a template had macro and meso-pores. The particle morphology of both surface and internal structures and adsorption performances were strongly affected by incremental addition of AKD. The prepared titania particles with AKD at 5 wt% showed a greater specific surface area, porosity, and rougher surface morphology than titania without AKD. The mass fractal dimension of the prepared titania with AKD at 5 wt% was 2.47. The prepared titania with AKD at 5 wt% showed a scale invariance between its surface and internal structures.

Acknowledgement

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Literature Cited


Table 1 Fractal dimension and surface area of the prepared titania

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface fractal dimension $D_s$ [—]</th>
<th>Mass fractal dimension $D_m$ [—]</th>
<th>Specific surface area $a_{BE T}$ [m$^2$/g]</th>
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</thead>
<tbody>
<tr>
<td>Titania with 0 wt% AKD</td>
<td>2.01</td>
<td>0.43</td>
<td>53.5</td>
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<tr>
<td>Titania with 5 wt% AKD</td>
<td>2.13</td>
<td>2.42</td>
<td>124</td>
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