VOCs Degradation Performance of TiO$_2$ Aerogel Photocatalyst Prepared in SCF Drying

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Abstract: Titania (TiO$_2$) aerogels were prepared by the sol-gel method using titanium(IV) chloride (TiCl$_4$) and subsequent supercritical fluid drying (SCD) to avoid collapse of the original gel structure. The characteristics of titania aerogels with varying epoxide/TiCl$_4$ ratios and amounts of water were analyzed using a BET surface analyzer, XRD, and FT-IR spectroscopy. VOCs, such as benzene, toluene, and $m$-xylene (BTX), were oxidized using the prepared titania aerogel; its performance was compared with that of commercially available TiO$_2$ (P-25, Degusa). The surface area, pore volume, and average pore diameter of the titania aerogel formed using 1,2-epoxybutane as an epoxide were significantly smaller than those obtained using propylene oxide. The titania aerogels with 6 mol of epoxides had high surface areas, pore volumes, and average pore diameters. As a result of photo-oxidation, the conversion of benzene reached ca. 70%; for the other reactants it reached ca. 60%. The conversion of BTX increased as the inlet concentration decreased. The reactivity of titania calcined at 600°C was greater than those of the sample calcined at 400 and 800°C. Water is required as a reactant for the oxidation of VOCs; the continuous consumption of hydroxyl radicals required replenishment to maintain catalyst activity. The activity ratio increased with the reaction time when enough water was present in the reactor.

Keywords: titania, sol-gel method, supercritical fluid drying (SCD), BTX, photo-oxidation

Introduction

Aerogels are of interest for applications as varied as thermal insulation, photocatalysis, and insecticides. The useful properties of aerogels result from their unusual combination of high porosity and small pore size. TiO$_2$ aerogels are most commonly prepared using supercritical fluid drying (SCD) of a wet gel. The wet gels are prepared using sol-gel synthetic methods. The method requires low temperature and low cost, and it can generally be performed under ambient conditions with general lab equipment, all of which make processing convenient. Sol-gel methods use metal alkoxide precursors that undergo catalyzed hydrolysis and condensation. However, some metal alkoxides are expensive and others are sensitive to moisture, heat, and light, making long-term storage difficult [1-3].

Volatile organic compounds (VOCs) lead to water and air pollution, and even indoor air pollution. The VOCs have a direct influence on indoor air pollution, and they stimulate human respiratory organs and eyes. Also, most VOCs are carcinogenic substances and cause sickness building syndrome (SBS). Among the methods used to oxidize VOCs, heterogeneous photocatalysis is one of the most attractive because of the mild conditions [4-6].

In this study, titania aerogels were prepared by the sol-gel method using titanium(IV) chloride (TiCl$_4$) and subsequent supercritical fluid drying (SCD) to avoid collapse of the original gel structure. The characteristics of titania aerogel with varying epoxide/TiCl$_4$ ratio and the amount of water were analyzed using a BET surface analyzer, XRD, and FT-IR spectrometer. VOCs, such as benzene, toluene, and $m$-xylene (BTX), were oxidized using the prepared titania aerogel; its performance was compared with that of commercially available TiO$_2$ (P-25, Degusa).
Experimental

Gel Formation by Sol-Gel Method
Wet gel formations were prepared using titanium(IV) chloride (Aldrich) as a metal precursor and methanol (Aldrich) as a solvent. Propylene oxide and 1,2-epoxybutane (Aldrich) were used as epoxides. The starting sol was prepared by mixing 1 mol of TiCl₄ and 30 mol of methanol. After vigorous stirring for 1 h, 2 mol of distilled water was added and the mixture was stirred for 30 min. The TiO₂ wet gel was prepared by adding the epoxy until the vortex disappeared completely. The wet gel was placed without oxygen at room temperature for 7 days. The textural properties and the gelling point were investigated with respect to the amount of epoxide (1 ∼ 10 mol) and distilled water (0 ∼ 10 mol).

Aerogel and Supercritical Fluid Drying Process
The wet gel was prepared using the sol-gel method; the solvent in the resulting wet gel was excluded by using the supercritical fluid drying process. A schematic illustration of the supercritical fluid drying apparatus is shown in Figure 1. The pressure vessel of stainless-steel was pressurized with CO₂ using a high-pressure gas booster; the temperature and pressure of the vessel were maintained to 60 °C and 3500 psi, respectively. The solvent was extracted by venting supercritical CO₂, and the reactor was heated up to 60 °C. The remainder of the solvent was extracted once more. TiO₂ aerogel was calcined at 400, 600, and 800 °C for 2 h, supplying O₂ at a rate of 95 mL/min.

Characterization of Aerogel
The surface area, pore volume, and pore size were investigated using a BET surface area analyzer (ASAP 2010, Micromeritics Co.). X-Ray diffraction (Norelco, Philips Electronic Instruments) was used to investigate the structure of the catalyst, employing CuKα (λ = 1.5405 Å) radiation. FT-IR (spectrum GX, Perkin Elmer Co.) spectroscopic analysis was performed to observe the behavior of the hydroxyl (OH) group with respect to the calcination temperature.

Photocatalytic Reaction
The experimental apparatus for the photocatalytic reaction is shown schematically in Figure 2. The photocatalytic experiments were carried out in a flow apparatus using a pyrex fixed-bed cylindrical reactor (ID: 23 mm; OD: 25 mm; L: 1 m). A porous frit at the inlet of the cylinder was used to distribute the inlet gaseous mixture. The reactor was placed horizontally inside an illuminating chamber in order to allow full irradiation of the catalyst. Four 40-W blacklight lamps (BLB-F40T10, Sankyo Denki Co.) were used as the light source. The light intensity on the photocatalyst surface under illumination with one lamp, measured using a UV radiometer (UCR-2 & UD-36, Topcon Co.) was 4824 µW/cm² in the range of wavelengths from 300 to 400 nm. The temperature in the reaction chamber was 39 °C.

This study was focused on testing the performance of the prepared TiO₂ aerogel and commercially available TiO₂ (P-25) in the photocatalytic degradation of VOCs. The reactants selected were benzene, toluene, and m-xylene. All solvents used were of reagent special grade.
### Table 1. Effect of H$_2$O Content on the Textural Properties of the Titania Aerogel

<table>
<thead>
<tr>
<th>H$_2$O/TiCl$_4$</th>
<th>6 mol of PO/TiCl$_4$</th>
<th>6 mol of EB/TiCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^a$SBET</td>
<td>$^b$V$_p$</td>
</tr>
<tr>
<td>1.5</td>
<td>138</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>0.91</td>
</tr>
<tr>
<td>4</td>
<td>111</td>
<td>0.49</td>
</tr>
<tr>
<td>6</td>
<td>115</td>
<td>0.39</td>
</tr>
<tr>
<td>10</td>
<td>109</td>
<td>0.35</td>
</tr>
</tbody>
</table>

$^a$ BET surface area (m$^2$/g); $^b$ total pore volume (cc/g); $^c$ average pore diameter (nm)

Figure 2. Apparatus for the photocatalytic oxidation of gas phase VOCs.

(Duksan Pure Chem. Co.). A definite amount of BTX was placed into the pyrex reaction tube. The pyrex reactor was filled with a glass bead, the surface of which was coated with TiO$_2$ photocatalyst by using a vacuum evaporation method. The masses of TiO$_2$ and the glass bead were 1.5 and 300 g, respectively.

The photocatalytic oxidation of BTX in a gas-phase stream was examined under variety of conditions, such as the effect of inlet concentration of reactants, the amount of H$_2$O, and the calcination temperature of the TiO$_2$ aerogels. The BTX concentration during the reaction process was analyzed using a GC-FID apparatus (HP 5890).

### Results and Discussions

#### Characterization of Titania Aerogel

Table 1 summarizes the surface areas, pore volumes, and average pore diameters for the titania aerogels with respect to the amount of H$_2$O. The prepared titania aerogels were calcinated at 600 °C. In the preparation of titania gels by the sol-gel method, the physical properties of titania depend on the preparation conditions, such as the water/alkoxide ratio, the calcination temperature, and the type of acid. It is well known that water plays an important role during the formation of the nucleus and the growth of the crystallites, and that the nucleus can be formed homogeneously when the water/alkoxide ratio is more than 10. It is well known that the formation of the nucleus can occur readily, rather than the growth of crystallites, as the water/alkoxide ratio increases and the crystallite size becomes small [7].

Titania aerogels cannot be prepared in non-aqueous solvents. Much solvent was extracted from the gel, and a colloidal-type gel was formed, above 6 mol of water, due to hydrolysis being faster than condensation. The surface area, pore volume, and average pore diameter of titania
Table 2. Effect of Epoxide on the Textural Properties of the Titania Aerogel

<table>
<thead>
<tr>
<th>H₂O/TiCl₄</th>
<th>PO/TiCl₄</th>
<th>EB/TiCl₄</th>
<th>After Calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>SₐBET</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>-</td>
<td>118</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>5</td>
<td>65.9</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>6</td>
<td>72.8</td>
</tr>
</tbody>
</table>

a BET surface area (m²/g); b total pore volume (cc/g); c average pore diameter (nm)

Figure 3. XRD patterns of TiO₂ aerogels formed at different calcination temperatures: (a) 400, (b) 500, (c) 600, (d) 700, and (e) 800 °C. Aerogel using 1,2-epoxybutane (EB) as a epoxide were significantly smaller than those of the sample prepared using propylene oxide (PO). It is likely that the epoxides in the sol-gel method act as proton scavengers. Also, the ring opening of propylene oxide through hydrolysis and condensation is faster than that of 1,2-epoxybutane. The gelling time decreased as the water content increased, and the color of the gel changed to opaque white, presumably because precipitation occurred when the gel was formed rapidly or slowly, and that the gel has fluidity. The strength of the gel was low when little water was used, but the gel shrank if too much water was used [1,2].

Table 2 summarizes the surface area, pore volume, and average pore diameter obtained with respect to the choice of epoxide. There was no gel formation below 4 mol of epoxide. These results indicate that epoxides cannot undergo further hydrolysis and condensation. Wet gels could be formed, however, above 7 mol before all of the epoxides were added. As shown in Table 2, the titania aerogels with 6 mol of epoxides had high surface areas, pore volumes, and average pore diameters. Figure 3 shows the XRD patterns of titania aerogels sintered at different calcination temperatures. The XRD patterns reveal that the major phases present are pure anatase at 400 °C, a mixture of anatase and rutile at 600 °C, and pure rutile phase at 800 °C. The heat-induced growth of crystallites of titania particles contributed to the increase of crystallinity because the higher ordering in the structure of titania particles makes the XRD peaks become

Figure 4. Photocatalytic conversion of BTX (50 ppmv inlet concentration).
sharper and narrower. The crystallinity of titania particles increased with increasing calcination temperature. This result indicates that the crystallite size increased with increasing calcination temperature. An increase in calcination temperature favors the anatase-to-rutile transition [8].

Photocatalytic Reaction of BTX
The inlet concentrations of BTX were 50, 100, and 200 ppmv, respectively, and the inlet amount of water was 1000 mg/m³. The temperature in the reflector was 39 °C, and the space time of the reactor was 52 s. Figures 4, 5, and 6 show the photocatalytic reactions with varying the inlet concentration of BTX. The conversion of benzene reached ca. 70 %; the other reactants reached ca. 60 %. The conversion of BTX increased as the inlet concentration decreased.

The conversion mediated by the TP (titania-propylene oxide, 6 mol of PO/TiCl₄, 2 mol of H₂O/TiCl₄) photocatalyst was ca. 10 % higher than those of P-25 and TE (titania-1,2-epoxybutane, 6 mol of EB/TiCl₄, 2 mol of H₂O/TiCl₄) presumably because the surface area of TP was larger than that of the other catalyst, and much water was adsorbed onto the surface of the catalyst. Figures 5 and 6 show a decreasing rate of photocatalytic activity at higher inlet concentrations. The photocatalytic conversion decreased as the inlet concentration increased because the reaction time of the photodegradation decreased. For benzene, the total conversion was higher than others in all inlet concentrations. Hydroxyl radicals from H₂O reacted to a greater extent with toluene and m-xylene than with benzene at the initiation step of the reaction. Benzene was attacked by hydroxyl radicals and water molecules on the photocatalyst surface.
These were due to prevent hole-electron recombination before the benzene attack. The photocatalytic degradation of benzene led to the formation of phenol. Other products of benzene photo-oxidation are 1,4-benzoquinone and hydroquinone. Thus, the conversion of benzene was low because the GC-FID peak was decreased. The results in this study are consistent with the results reported by d’Hennezel and coworkers [9]. The photocatalytic degradations of toluene and \( m \)-xylene involved abstraction from the methyl group leading to benzyl radicals. Thus, the methyl groups of aromatic radical cations dissociated by methyl atom dissociation energy. Our results are consistent with the results reported by other researchers [9,10].

**Effect of Calcination Temperature on the Photocatalytic Reaction**

Figure 7 shows the effect of the photocatalytic reaction with respect to the calcination temperature. The conversion of benzene using TP photocatalysts (6 mol of PO/TiCl\(_4\), 2 mol of H\(_2\)O/TiCl\(_4\)) that had been calcined at 400, 600, and 800 °C reached 65, 70, and 55 % respectively. The surface areas of the titania aerogels calcined at 600 and 400 °C were 150 and 180 m\(^2\)/g, respectively. However, the conversion of titania aerogel calcined at 600 °C was ca. 10 % higher than that of the sample calcined at 400 °C.

According to Figure 3, the XRD patterns of the titania aerogel revealed that the main phases present were pure anatase at 400 °C, a mixture of anatase and rutile at 600 °C, and pure rutile phase at 800 °C. One of the reasons why the anatase-type titania is more photoactive than the rutile-type may lie in the differences in their so-called energy band structures. The shift of the band-gap absorbance from the near-UV region increases the effectiveness of the rutile phase. This feature indicates that the anatase-type titania has a larger light-absorption capacity than rutile-type titania, which gives rise to its greater oxidizing power by readily producing holes. These holes can react with water to produce the highly reactive hydroxyl radical that plays an important role in breaking down the organic compounds [11]. The permeation of
light by anatase was decreased as a result of the small particle size. On the other hand, the photo-efficiency of the rutile phase decreased due to its large particle size. Thus, the photocatalytic activity of the mixture of anatase and rutile at 600 °C was increased because of a decrease of the screen effect [12,13].

**Effect of H$_2$O on the Photocatalytic Reaction**

Numerous studies have revealed the effects of water on photocatalytic reactions. The effect of water in gas phase photocatalytic reaction depends on the reactants. It has been known that water vapor strongly inhibits the oxidation of isopropanol, trichloroethylene, and acetone, but enhances the oxidation of toluene and formic acid, while having no effect on 1-butanol oxidation [9,14-16]. In the presence of water vapor, the hydroxyl radicals formed on the illuminated TiO$_2$ not only can directly attack VOC molecules but also can suppress electron-hole recombination [17,18]. Hydroxyl groups or water molecules behave as hole traps, forming surface-adsorbed hydroxyl radicals. However, under higher-humidity conditions, the water molecules could compete with the VOC molecules on the catalyst surface sites during the adsorption [9,14,17].

Figure 8 shows the effect of water vapor on the conversion of BTX. The conversion of BTX was enhanced by water, but low conversion (ca. 30 %) occurred in the absence of water. On the other hand, the activity ratio increased with increasing reaction time when sufficient water was present in the reactor. This observation suggests that the photodecomposition requires the photogenerated holes to be scavenged by adsorbed water or hydroxyl radicals. This result also indicates that the product of this reaction is the hydroxyl radical, which can then initiate oxidation through hydroxylation of the aromatic ring. As the reaction proceeds, hydroxyl radicals and water molecules are involved in further reaction steps that lead to the eventual opening of the ring [9,19].

**Conclusions**

Titania aerogels cannot be prepared in non-aqueous solvents. Much solvent was extracted from the gel and the colloidal-type gel was formed above 6 mol of water because of hydrolysis being faster than condensation. The surface area, pore volume, and average pore diameter of the titania aerogel formed using 1,2-epoxybutane as the epoxide were significantly smaller than those obtained using propylene oxide (72.8 m$^2$/g, 20.9 nm, and 0.37 cc/g; cf. 150 m$^2$/g, 24.3 nm, and 0.37 cc/g). The titania aerogels prepared with 6 mol of epoxides had high surface areas, pore volumes, and average pore diameters. The conversion of VOCs increased as the inlet concentration decreased and the amount of H$_2$O increased. Also, the photocatalytic oxidation of BTX increased in the order TP > TE > P-25. The conversion of benzene was the highest at 1000 mg/m$^2$ H$_2$O and 50 ppmv inlet concentration. The reactivity of the reactants decreased in the order benzene > toluene > m-xylene. The conversions reached similar steady-state values, and the color of the photocatalysts changed from white to brown after the photo-oxidation of BTX. The continuous consumption of hydroxyl radicals required replenishment to maintain the catalyst activity. In terms of the calcination temperature, the reactivity of the titania sample calcined at 600 °C was greater than those of the samples calcined at 400 and 800 °C. Water was required as a reactant for the oxidation of these VOCs. The activity ratio increased upon increasing the reaction time when a sufficient amount of water was present in the reactor. These results were due to the production of hydroxyl radicals from H$_2$O.

**Acknowledgment**

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**References**