Technical Note

Photocatalytic oxidation of gas-phase elemental mercury by nanotitanosilicate fibers

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Abstract

Photocatalytic fibers were generated from the continuous evaporation of titanium tetraisopropoxide with tetraethyl orthosilicate through a flame burner. The morphology, the crystal form, and the components of the nanotitanosilicate fibers were analyzed by Raman spectroscopy, Field emission-scanning electron microscope, X-ray diffraction, and Brunauer–Emmett–Teller surface area analysis. The nanotitanosilicates prepared by three different carrier gases (air, N₂, and Ar) were tested for their photocatalytic ability to remove/oxidize gas-phase elemental mercury. Under UV black light, the Hg⁰ capture efficiencies were 78%, 86%, and 85% for air, N₂, and Ar, respectively. For air, the value was close to 90%, even under household fluorescent light. The Hg⁰ capture efficiency by nanotitanosilicate was measured under fluorescent light, UV black light, and sunlight.

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Keywords: Photocatalytic fiber; Diffusion flame burner; Nanotitanosilicate; Mercury removal

1. Introduction

In recent years, various applications of TiO₂ in many different types of catalytic devices, solar cells, and other optoelectronic devices have been demonstrated (Taramasso et al., 1983; Regan and Grätzel, 1991; Hoffmann et al., 1995). The effectiveness of these systems depends on the photocatalytic properties of TiO₂, which are in turn strongly related to its crystal structure and grain size. In most cases, TiO₂ in the anatase phase appears to be most useful, due to its high photocatalytic activity and physico-chemical stability (Rao et al., 1980; Nishimoto et al., 1985).

Nanocrystalline TiO₂ grains grow at relatively lower temperatures and undergo phase transformation, which limits their application in many situations accompanying high temperature (Anderson et al., 1988; Bhave, 1991). On the other hand, the fibrous membrane with high thermal stability allows for gas separation at high temperatures. In combination with a chemical reaction, the membrane acts as a catalyst, as well as a selective barrier to remove one of the formation components (Ezzo et al., 1979; Brink and Scherer, 1990; Makishima et al., 1990; Bhave, 1991). Therefore, as with the titania membrane systems, it is necessary to: (1) generate the TiO₂-compounds at certain conditions to prevent any further phase transformations once they have been formed and (2) to prepare the compounds in fibrous form with a relatively high surface area. Recent studies suggest that silica-modified titania exhibit high thermal stability (Iwamoto et al., 2000). Also, several researchers have reported the fabrications of dense TiO₂ in various configurations such as: (1) titania nanoribbons with a size range of 30–200 nm under hydrothermal conditions, from amorphous titania or titanium precursors in a basic medium (Yuan et al., 2002), (2) amorphous titania nanofibers, electrospun from titanium tetraisopropoxide (TTIP) mixed with acetic acid and high molecular weight polyvinylpyrrolidone (Li and Xia, 2003), and (3) titania films with micrometer pore size, by electrostatic sol-spray deposition using TTIP (Nomura et al., 2003). Little has been reported regarding the morphogenesis of column-shaped nanotitanosilicate, prepared using a flame reactor.

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Meanwhile, many researchers have been seeking effective ways to capture mercury from combustion flue gases (Korpiel and Vidic, 1997; Hsi et al., 2001; Jurng et al., 2002), due to their high toxicity, tendency to bio-accumulate, and difficulty to control. In previous studies (Wu et al., 1998; Lee et al., 2001), a very high Hg\textsuperscript{0} capture efficiency by commercially available TiO\textsubscript{2} powders, under various light sources have been reported, using UV light (black and sterilizing, >99%), fluorescent light (home-style, >99%), and visible blue light (>400 nm, ~85%). These studies showed that a far stronger bond formed between mercury and TiO\textsubscript{2} under photocatalytic oxidation. For the elemental mercury photo-oxidation process by TiO\textsubscript{2}, the mechanistic illustration has been introduced (Lee and Hyun, 2006).

This study introduces a novel method for preparing photocatalytic fibers by the controlled growth of column-shaped nanotitanosilicate. Also, we investigate their physical and chemical properties, specifically their ability to photo-oxidize and capture gas-phase elemental mercury in a well-controlled gas system (Hg\textsuperscript{0} + air + carrier gas).

2. Experimental

2.1. Nanotitanosilicate fiber preparation

A schematic of the experimental setup for the preparation of the nanotitanosilicate fiber is shown in Fig. 1a. A diffusion flame reactor was designed to generate the nanotitanosilicate particles, and a slide glass plate (75 × 25 mm) was used to collect and grow the photocatalytic fibers. Different ratios of TTIP and tetraethyl orthosilicate (TEOS) mixture (2:1, 4:1, 10:1, and 12:1, by weight) were introduced into the flame system by a variably selected carrier gas. Flow rate of fuel (LPG), oxidant (O\textsubscript{2}), sheath gas (N\textsubscript{2}), and carrier gas were precisely controlled at 250, 400, 500, and 2000 sccm, respectively. In Fig. 1a, precursor solution was vaporized and carried with carrier gas (air, N\textsubscript{2}, and Ar) through the nozzle located in the center. The sheath gases, O\textsubscript{2} and N\textsubscript{2}, were passed through the nozzles located in the 2nd and 3rd layer from the center, respectively. LPG was passed through the space between nozzles. The temperature of the water bath containing TTIP was maintained at 50°C. The mixture of precursors was dynamically stirred at room temperature for 20 min. The glass plate was rotating horizontally at the speed (22–23 rpm) enough to avoid melting and/or deforming, passing through the center of the flame (1450–1550°C). The nanotitanosilicate particles were collected on the lower surface of the glass plate, only 3 cm above the top of the burner. In order to collect 40 mg, about 90 h was required.

2.2. Characterization of nanotitanosilicate fiber

The crystallinity of the samples was checked with both a Rigaku X-ray diffractometer (XRD) with a Cu K\textalpha\textsubscript{r} radiation source (λ = 0.15405 nm) and Raman spectroscopy (T64000, Jobin-Yvon, France) with a 514.532 nm laser Ar-ion (2 mW on sample). Analysis of the morphology and size of the prepared nanotitanosilicate fibers was conducted by SEM (JSM5410LV, JEOL, Japan), after coating the collected samples with a gold-layer (~20 nm) in a cathodic evaporator. The BET surface area of nanotitanosilicate fibers was determined from nitrogen adsorption–desorption obtained at 77 K by a Micromeritics\textsuperscript{®} ASAP 2020.

2.3. Photoreactivity (Hg\textsuperscript{0} capture efficiency) of nanotitanosilicate fibers

Two nanotitanosilicate-coated glass plates, prepared by using the diffusion flame reactor (Fig. 1a), were placed side
by side in a quartz-covered flat-type photochemical reaction cell (inner dimension; 75 × 50 mm). A complete reaction system is shown in Fig. 1b.

Mercury vapor was introduced into the system through a photochemical reaction cell by passing N₂ at a precisely controlled flow rate (MKS Mass-Flo Controller, MKS Instruments, Inc.) above liquid elemental mercury (99.9%, Aldrich), contained in a temperature controlled gas-washing bottle. The flow rate of N₂ through the Hg containing gas-washing bottle in the water bath was 50 sccm; water bath temperature was 20 °C. The range of Hg inlet concentration tested was 400–500 µg mL⁻¹.

The gas-phase elemental mercury concentration from the photochemical reaction cell was constantly monitored in real-time by the on-line Hg⁰ analyzer (VM3000, Mercury Instruments, Germany). The light source was supplied only after the mercury concentration reading had stabilized, and the outlet mercury concentration was measured.

Wavelength distribution and the corresponding intensity were measured for the fluorescent light (2 × FL40D, Osram-Korea, Korea) and UV black light (2 × TLD36w/08, Philips, Netherlands) at a distance of photochemical reaction cell from the light source.

3. Results and discussion

3.1. Characterization of nanotitanosilicate fibers

Nanotitanosilicate fibers are synthesized by the evaporation of TEOS with TTIP by atomization method at 1450–1550 °C, and the proposed mechanism is shown in Fig. 2. Raman spectroscopy results of the samples, all prepared using air as a carrier gas at various TTIP to TEOS ratios, are shown in Fig. 3. A crystal form was only observed for the TTIP/TEOS ratio of 10:1 and 12:1, and not for the TTIP/TEOS ratio of 2:1 and 4:1, indicating the crucial dependence of crystallite growth on TTIP/TEOS ratio. Five distinct Raman peaks, located at 142.2, 196.1, 396.3, 518.5, and 638.1 cm⁻¹, were identified for TTIP:TEOS of 10:1 and 12:1. However, for TTIP:TEOS of 2:1 and 4:1, the samples did not show crystal structures due to the increased amount of silica.

Fig. 2 shows the field emission-scanning electron microscope (FE-SEM) images of the fibers prepared with three different carrier gases (air, N₂, and Ar). The diameters of the fibers are in the range of 50–100 nm, and their lengths are typically up to several tens of μm. A relatively rough and coarse surface was observed, probably caused by the volume shrinkage during the collection process due to further heating and densification of the readily deposited fiber by the high temperature flame. The results in Fig. 4 suggested that the surface areas of the fiber samples correspond to the exterior surfaces of nanotitanosilicate fibers and that no micropores were formed in the interlayer. The measured BET surface areas of nanotitanosilicate fibers corresponding to the carrier gas used (air, N₂, and Ar) were 45, 78, and 126 m² g⁻¹, respectively (Table 1).

3.2. Photoreactivity (Hg⁰ capture efficiency) of nanotitanosilicate fibers

In Fig. 5, the XRD spectra of column-shaped nanotitanosilicates show the existence of both anatase and rutile phases. Three different carrier gases (air, N₂, and Ar) were used for comparison, maintaining the TTIP/TEOS ratio at 12–1. This ratio was selected after considering the Raman
analysis results previously discussed (Fig. 3). Such crystallinity strongly affected the structural and electronic properties of the photocatalyst.

The samples were then tested for their ability to oxidize Hg⁰, generally referred to as Hg⁰ capture efficiency, in a specially designed nanotitanosilicate photochemical reactor. The Hg⁰ capture efficiency (η) was based on inlet/outlet gas-phase Hg⁰ concentrations: 

$$\eta = \frac{Hg_{in} - Hg_{out}}{Hg_{in}}$$

A description of the reaction between the column-shaped nanotitanosilicate particle and Hg⁰ has been suggested by previous studies (Wu et al., 1998; Lee et al., 2001). The positive holes may result in OH radical forma-

![Fig. 3. Raman spectra of nanotitanosilicate fibers using air as a carrier gas (TTIP:TEOS ratios of: (a) 2:1, (b) 4:1, (c) 10:1, and (d) 12:1).](image)

![Fig. 4. FE-SEM images of nanotitanosilicate fibers (TTIP/TEOS carried by (a) air, (b) N₂, and (c) Ar).](image)

![Fig. 5. X-ray diffraction patterns of nanotitanosilicate fibers (TTIP:TEOS ratios of 12:1 carried by (a) air, (b) N₂, and (c) Ar; A: antase, R: rutile).](image)

![Table 1 Hg⁰ removal efficiency by the nanotitanosilicate fibers under different light sources](table)

<table>
<thead>
<tr>
<th>Carrier gas used for nanotitanosilicate fibers (TTIP:TEOS = 12:1)</th>
<th>Light sources</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>fluorescent</td>
<td>88</td>
</tr>
<tr>
<td>N₂</td>
<td>UV black</td>
<td>8</td>
</tr>
<tr>
<td>Ar</td>
<td>The sun</td>
<td>8</td>
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</table>

<table>
<thead>
<tr>
<th>Light sources</th>
<th>UV black</th>
<th>The sun</th>
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<tr>
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<td>51</td>
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<tr>
<td>UV black</td>
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<td>17</td>
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<td>The sun</td>
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</tr>
<tr>
<td>N₂</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 6 shows the plot of real-time Hg⁰ concentration at the exit of the reaction cell of nanotitanosilicate fibers prepared with three different carrier gases, air, N₂, and Ar under various light sources: (a) fluorescent, (b) UV black,](image)
All fiber samples were prepared under the same conditions except for the type of carrier gas used. The ratio of TTIP to TEOS was maintained at 12–1, and the amount of sample tested was always 40 mg. To verify the fact that elemental mercury was actually removed by chemisorption onto the photocatalytic fiber surface and not simply discharged into the gas-phase in the oxidized form, the simulated flue gas out of the photochemical reactor was sampled using the Ontario Hydro Method and then analyzed. No oxidized form of mercury was detected.

The results in Table 1 show the following order of decreasing photoreactivity for the carrier gases tested: air, N₂, and Ar. Photocatalytic fibers prepared with air as the carrier gas exhibited the highest Hg⁰ capture efficiency of 88% under the fluorescent light (2 × 36 W). However, in the case of N₂ and Ar as carrier gases, the Hg⁰ capture efficiency was less than 10% under the same fluorescent light. On the other hand, under UV black light with wavelengths of 300–400 nm, the Hg⁰ capture efficiencies were relatively high for all three carrier gases (air: 78%, N₂: 86%, and Ar: 85%). The low Hg⁰ capture efficiencies of N₂- and Ar-derived nanotitanosilicate under the fluorescent light (which was also observed under the sunlight) are due to the lack of a rutile phase. This is in contrast to the case for air (Fig. 5), since the rutile phase better corresponds to light sources with longer wavelengths (Lee et al., 2004). It also explains the relatively high Hg⁰ capture efficiency of air-derived nanotitanosilicate, exhibiting both anatase and rutile phases under fluorescent light and sunlight. Values for Hg⁰ capture efficiency, listed in Table 1, could be increased (as high as 100%) by increasing the amount of nanotitanosilicate used in the photochemical reactor (Lee et al., 2004). Values in Table 1 were used in this study only to compare the relative Hg⁰ removal effectiveness between the tested samples.

Values for Hg⁰ capture efficiency, listed in Table 1, could be increased (as high as 100%) by increasing the amount of nanotitanosilicate used in the photochemical reactor (Lee et al., 2004). Values in Table 1 were used in this study only to compare the relative Hg⁰ removal effectiveness between the tested samples. A relatively high Hg⁰ capture efficiency of amorphous TiO₂ was observed under UV light probably due to large moisture contents (relative humidity of more than 90% during particle collection). It was previously reported that the hydrated forms of amorphous titania, TiO₂ nH₂O, should be noted as a significant factor in promoting the greater concentrations of Ti³⁺ at the surface and higher photoreactivity rates for H₂ evolution (Zhang and Maggard, 2007). In addition, according to the previous reports (Kaneko and Okura, 2002; Zhang et al., 2007; Zhang and Maggard, 2007), amorphous TiO₂ has greater band gap energy of 3.27 eV than rutile and anatase TiO₂, which has band gap energy of 3.0 and 3.2 eV, respectively. Since UV black light can still provide enough energy for the band gap of the amorphous nanotitanosilicate fibers, much higher Hg⁰ removal efficiency was observed even for the photocatalytic fibers prepared with N₂ and Ar as carrier gases.

4. Conclusions

In summary, we developed a new method for the preparation of photocatalytic fibers from column-shaped nanotitanosilicate by a diffusion flame reactor, using a mixture of TTIP and TEOS. First, the mixture of TTIP and TEOS is vaporized and carried into the flame system at 1450–1550 °C in the presence of fuel (LPG), oxidants (O₂), sheath gas (N₂), and different types of carrier gas (air, N₂, and Ar). Vapors are then condensed and particles are charged into the gas-phase in the oxidized form, the simulated flue gas out of the photochemical reactor was sampled using the Ontario Hydro Method and then analyzed. No oxidized form of mercury was detected.
formed by nucleation. The particles are then self-assembled to form nanotitanosilicate fibers during which carbon dioxide and hydrogen molecules are removed. The resulting fibers have high thermal stability and a large number of terminal oxygens, which makes them suitable for photocatalytic materials.

Furthermore, the photocatalytic activities of various nanotitanosilicate samples were evaluated by observing the Hg\textsuperscript{0} oxidation capacity, generally referred to as the Hg\textsuperscript{0} capture efficiency. The Hg\textsuperscript{0} capture efficiency was obtained for all three types of carrier gas (air, N\textsubscript{2}, and Ar). The highest Hg\textsuperscript{0} capture efficiency (88\%) was achieved for the case of air under household fluorescent light, which is low-cost and easily maintainable.

Acknowledgement

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References

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