Abstract Adsorption and photocatalytic characteristics of a new composite type of silica bead supported with calcium phosphate and TiO$_2$ for aldehydes removal were evaluated. The bead was suitable for the adsorption of acetaldehyde, though the adsorption efficiency of the bead for formaldehyde was slightly lower than that of other beads tested. The removal with this new bead for acetaldehyde is superior to that with silica bead supported with only TiO$_2$ in the lighting up and under a high space velocity condition. The removal of formaldehyde was complete by composite effects of adsorption and photocatalytic decomposition using the bead under regular space velocity conditions.

INTRODUCTION

Acetaldehyde is a typical odor compound emitted from thermal degradation or incomplete burning of polymers and various organic compounds. Formaldehyde is one of hazardous air pollutants, eye irritant and suspected carcinogen. Although photocatalytic treatment of these aldehydes using TiO$_2$ have been reported$^{1-5}$, rapid and efficient removal methods have not been established. Fukaya et al. reported a preparation method of silica bead supported with TiO$_2$$^6$. In the previous papers$^7-8$, we reported on an
adsorption and photocatalytic decomposition of dimethyl sulfide using silica bead supported with TiO₂ (TiO₂/SiO₂). The bead was efficient for the treatment of gaseous odor compounds containing sulphur, but not enough for removal of acetaldehyde in air. In this paper, we report on a new composite type of silica bead supported with calcium phosphate and TiO₂, and its adsorption and photocatalytic characteristics for aldehydes treatment.

EXPERIMENTAL

A silica bead supported with calcium phosphate and TiO₂ (CP/TiO₂/SiO₂) was prepared by the following process: Tricalcium phosphate was dissolved in a 0.22 mol⋅dm⁻³ phosphoric acid and the solution was mixed with TiO₂/SiO₂ bead prepared by the process described in the previous paper⁷. A 0.25 mol⋅dm⁻³ sodium hydroxide solution was added to the mixture for neutralization. Thereafter, the solid part of the mixture was separated and dried at 110 °C for 2hr.

The particle size of the bead is 3–4mm in diameter. Specific surface area and average pore diameter were measured by a Fiji Silisia Chemistry. Energy dispersive X-ray(EDX) spectra were measured with a Japan Phillips EDAX DX–4. X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex diffractmeter using Cu Kα radiation.

Adsorption test of formaldehyde or acetaldehyde in air was performed at dark space in a 5-L volume of Tedlar bag which was filled with each gaseous aldehyde and contained 5g of each bead. The experimental apparatus for photocatalytic reaction was described in the previous paper⁷. Photocatalytic degradation of formaldehyde or acetaldehyde was performed at a space velocity of 67hr⁻¹. The light source used was a black-light–type lamp(Toshiba Lightec Co., 2W). The photocatalytic vessel was covered with aluminium foil to shut off the outside light. Sample gas was prepared with pure air(Nippon Sanso Co.). Acetaldehyde in inlet and effluent gas was measured by a gas chromatograph(Shimadzu GC–15A) equipped with flame ionization detector(FID). Formaldehyde and CO₂ in inlet and effluent gas were measured by a gas chromatograph(Hitachi 663) equipped with methanyzer followed by FID. Organic acids collected in water at the outlet of the vessel
after the reaction were measured by a high performance liquid chromatograph (Shimadzu organic acid analysis system).

RESULTS AND DISCUSSION

Characterization of CP/TiO$_2$/SiO$_2$ bead

Characteristics of TiO$_2$/SiO$_2$ and CP/TiO$_2$/SiO$_2$ beads are shown in Table 1. Average pore diameters of the beads were equivalent to each other. The specific surface area of CP/TiO$_2$/SiO$_2$ bead was higher than that of TiO$_2$/SiO$_2$ bead.

EDX spectra of the inner of CP/TiO$_2$/SiO$_2$ bead are shown in Figure 1. The elements of Ca and P were detected at both surface and inner of the bead. It was recognized that some kind of calcium phosphates exists with TiO$_2$ in the pore and at the surface of the bead. The XRD pattern of the precipitated product from tricalcium phosphate reagent by the same process as CP/TiO$_2$/SiO$_2$ bead preparation is shown in Figure 2. The product was a mixture of brushite (CaHPO$_4$$\cdot$2H$_2$O) and monetite (CaHPO$_4$). Therefore, the calcium phosphate formed on the CP/TiO$_2$/SiO$_2$ bead must be also brushite and monetite.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area / m$^2$.g$^{-1}$</th>
<th>Ave. pore dia. / nm</th>
<th>TiO$_2$ content / %</th>
<th>Surface</th>
<th>Inner</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/SiO$_2$</td>
<td>192</td>
<td>9.5</td>
<td>18.2</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>CP/TiO$_2$/SiO$_2$</td>
<td>250</td>
<td>10.0</td>
<td>10.2</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

Comparison of adsorption efficiencies of aldehydes

Adsorption efficiencies of silica bead, TiO$_2$/SiO$_2$ bead and CP/TiO$_2$/SiO$_2$ bead for formaldehyde and acetaldehyde are shown in Table 2. Silica bead and TiO$_2$/SiO$_2$ bead adsorbed completely gaseous formaldehyde in 30min, and the adsorption efficiency of CP/TiO$_2$/SiO$_2$ bead for formaldehyde was 89% after 30min. On the other hand, the order
of adsorption efficiency for acetaldehyde was CP/TiO$_2$/SiO$_2$ bead > TiO$_2$/SiO$_2$ bead > silica bead. That is, CP/TiO$_2$/SiO$_2$ bead was most suitable for acetaldehyde adsorption, though the adsorption efficiency of the bead for formaldehyde was slightly lower than that of the other two kinds of beads.

FIGURE 1  EDX spectrum of the inner of CP/TiO$_2$/SiO$_2$ bead.

FIGURE 2  XRD pattern of the solid produced from tricalcium phosphate.
TABLE 2 Adsorption efficiency of silica and photocatalytic beads for aldehydes.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Adsorption efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silica bead</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>100</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>59</td>
</tr>
</tbody>
</table>

Formaldehyde:15ppm, Acetaldehyde:18ppm, Standing time:30min

Photocatalytic removal of aldehydes

The comparison of acetaldehyde removal between CP/TiO$_2$/SiO$_2$ bead and TiO$_2$/SiO$_2$ bead in the lighting up condition at a space velocity (SV) of 2,010 hr$^{-1}$ is shown in Table 3. The results show that the removal with CP/TiO$_2$/SiO$_2$ bead for acetaldehyde is superior to that with TiO$_2$/SiO$_2$ bead under the high velocity condition.

TABLE 3 Removal of acetaldehyde using photocatalytic beads in the lighting up condition.

<table>
<thead>
<tr>
<th>Material</th>
<th>Removal of acetaldehyde / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5min</td>
</tr>
<tr>
<td>TiO$_2$/SiO$_2$</td>
<td>80</td>
</tr>
<tr>
<td>CP/TiO$_2$/SiO$_2$</td>
<td>94</td>
</tr>
</tbody>
</table>

Acetaldehyde:48.5ppm, SV=2,010hr$^{-1}$

The removals of acetaldehyde and formaldehyde using CP/TiO$_2$/SiO$_2$ bead in the lighting up condition at various space velocities are shown in Figure 3. The removal of formaldehyde was 100% as well as that of acetaldehyde under the conditions. That is, the removal of formaldehyde was complete by composite effects of adsorption and photocatalytic decomposition using CP/TiO$_2$/SiO$_2$ bead under mild velocity conditions, though the adsorption efficiency of the bead for formaldehyde was slightly lower than that of other beads. Figure 4 shows the continuous removal for acetaldehyde and formaldehyde using CP/TiO$_2$/SiO$_2$ bead in the lighting up condition. The removal for each aldehyde was 100% up to at least 210L of passing gas volume at SV=67hr$^{-1}$.

Decomposition products of acetaldehyde
The photocatalytic decomposition products of acetaldehyde in effluent gas using CP/TiO$_2$/SiO$_2$ bead were mainly CO$_2$ and trace amounts of formic and acetic acid. The removal of acetaldehyde and the conversion to CO$_2$ is shown in Figure 5. The conversion

![Diagram](image)

**FIGURE 5** Photocatalytic removal of acetaldehyde and production of CO$_2$. 

---

The photocatalytic decomposition products of acetaldehyde in effluent gas using CP/TiO$_2$/SiO$_2$ bead were mainly CO$_2$ and trace amounts of formic and acetic acid. The removal of acetaldehyde and the conversion to CO$_2$ is shown in Figure 5. The conversion
to CO$_2$ were in the range 1.2–6.3 %. From this result, it is assumed that the removal of acetaldehyde is mainly due to adsorption effect and photocatalytic decomposition proceeds little by little by the diffusion of acetaldehyde molecule from the adsorption site to photocatalytic site in CP/TiO$_2$/SiO$_2$ bead.

REFERENCES