

Improved photocatalytic activity of zeolite- and silica-incorporated TiO₂ film

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Abstract

Porous TiO₂ film was prepared by sol–gel method from TiO₂ sol containing polyvinylpyrrolidone (PVP). Photocatalytic activity of the film was evaluated by the elimination rate of ethylene. Several adsorbents including zeolite and silica powders were incorporated into the TiO₂ film. All the adsorbents enhanced the activity. The optimum adsorbent content was 0.005–0.01 g/ml of the coating sol solution. Silica provided better activity than zeolite. At high humidity and in dry air the activity decreased.

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1. Introduction

Photocatalytic air and water purification using TiO₂ is a promising environmental technology and its practical applications are in progress. Yet the improvement of the activity is required to further promote its practical use and to develop new applications. Incorporation of adsorbent into TiO₂ has been considered a practical way to enhance the activity. It not only collects pollutants from dilute solution or open air to the vicinity of TiO₂ active site, but also retains them to be degraded by additional illumination. Many studies have been reported on adsorbent-incorporated TiO₂ [1–10]. Most of those works are carried out with TiO₂ powder. However film is more convenient than powder for practical use. One of the authors previously reported on zeolite (powder)-embedded TiO₂ film [11]. This film was effective for benzene degradation. The present study aims at the further improvement of the activity by incorporating different adsorbents. In addition the effect of humidity on these adsorbent-incorporated films was studied for its importance from practical viewpoint. Although the effect of humidity on the degradation of

gaseous compound on plain TiO₂ has been reported by several authors [12–16], very few studies were reported on the humidity effect in the presence of adsorbent to the best of our knowledge [11]. The degradation of ethylene was investigated to evaluate the photocatalytic activity. Ethylene is reactive and flammable gas. It causes several health hazards such as headache, dizziness, fatigue and skin problem, and is on the hazardous substance list in the US and other countries. Ethylene elimination is also of industrial significance for keeping fruits fresh during the storage. The results obtained in this study can be applied to other toxic gaseous chemicals.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP) (average mW = 360,000) was purchased from Wako Pure Chem. Co. Ethylene (99.5% purity) is a product of Japan Oxygen Co. Zeolite (HSZ320 and HSZ870), silica OX50 and QS-09 were supplied by Toso Co., Nihonaerosil and Tokuyama Corp., respectively. TiO₂ is TP-2 (anatase) purchased from Fujititan [17]. The characteristics of zeolite, silica and TiO₂ are listed in Table 1.

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Table 1
Characteristics of adsorbents

Adsorbent	Si/Al	Specific surface area (m ² /g)	Diameter (nm)
Zeolite HSZ320	5.4	695	
Zeolite HSZ870	190	241	
TiO ₂ TP-2		17.3	260
Silica OX50		50	40
Silica QS-09		88	5–50

2.2. Preparation of TiO₂ film

TiO₂ sol was prepared by adding a mixture of 7 ml ethanol and 0.4 ml of 2.3 mol/l HCl to 5.1 g titanium tetraisopropoxide dropwise, while stirring magnetically. Then PVP was added (0, 20 and 40 wt.% for TiO₂) to the sol and stirred for 2 h. 0.8 ml of this mixture was placed on a 200 mm × 10 mm Pyrex glass plate and spin-coated at different rotation speeds (2000, 3000 and 5000 rpm). The coated plate was calcined at different temperatures (550, 600 and 650 °C) for 1 h after the temperature was raised to the fixed value at the rate of 5 °C/min.

Adsorbent-incorporated film was prepared by the same procedure except that the different amounts of zeolite, silica or titanium dioxide powder were added to 4 ml of the above mixture before coating. The coated plate after the calcination was smoothed by a cotton cloth in the case that the surface is coarse due to unsettled adsorbent at the higher content, washed by distilled water and dried at 100 °C for 1 h. The adsorbent content was expressed by gram of adsorbent initially added to millilitre of sol solution.

2.3. Degradation

A reactor used for the photocatalytic degradation of ethylene was illustrated in Fig. 1. A 6 W black lamp placed in a quartz protection tube was used as a light source, and its intensity in 330–390 nm range was 2.0–2.5 mW/cm² on the outside surface of the protection tube. A sample plate was placed below the

lamp in the reactor. To prepare ethylene sample of fixed concentration, the whole system of the reactor was evacuated and ethylene diluted by air was introduced, and then leaked to air. The initial ethylene concentration was 8.5×10^{-7} mol in 631 ml of reactor volume (1.35×10^{-6} mol/l). The gas was circulated in the dark for at least 1 h. The gas sample was taken periodically by a syringe before and after the illumination and was subjected to the analysis by a Shimadzu GC 9A. Adsorption to the film was estimated from the difference between control value in the absence of TiO₂ and the average of those before illumination.

2.4. Humidity control

The humidity was adjusted as follows. For low humidity (dry) the reactor was evacuated and then leaked to air through a glass tube filled with silica gel. This procedure was repeated three times. For high humidity water placed in an attached cell (d in Fig. 1) was bubbled by circulating the air in the reactor for 1 h and then ethylene gas was introduced. Relative humidity values measured at the place of the leaking valve (e in Fig. 1) were around 63% for high humidity and 28% for low humidity at 19 °C, while ambient humidity was roughly 43% at the same temperature (average value measured in winter by controlling the temperature).

2.5. Analysis of intermediates

2.1×10^{-3} mol/l ethylene was illuminated for 4 h and then bubbled in 2 ml water in an attached cell (d in Fig. 1) for 1 h. This solution was analyzed for organic acid and carbonate ion by Yokogawa IC7000. Formaldehyde was analyzed by a colorimetric method using 2,4-dinitrophenylaldehyde as a coloring agent [18].

3. Results and discussion

3.1. TiO₂ film

TiO₂ film was prepared under various conditions: different rotation speeds; PVP concentrations; and calcination temperatures. Crack-free films were produced at the rotation speeds of 2000 and 3000 rpm with 40% PVP and at 3000 rpm with 20% PVP. In the absence of PVP crack-free film was obtained only at 5000 rpm. The film thickness decreased with decreasing PVP concentration, increasing rotation speed and rising calcination temperature: a film prepared with 40% PVP and at 3000 rpm and at 600 °C was about 0.26 μm thick and one prepared under the same conditions but with 20% PVP was about 0.21 μm. General trend is that the higher PVP concentration and larger rotation speed provide the better quality film. These observations suggest that PVP suppresses cracking of the film.

Photocatalytic activities of these films were evaluated by measuring ethylene degradation rate. Fig. 2 demonstrates that the degradation rate was accelerated by the presence of TiO₂ film and its activity was improved by the addition of PVP to the coating sol: 40% PVP was better than 20% (Fig. 2). The effect of PVP may be due to the porous surface formed after PVP burnout

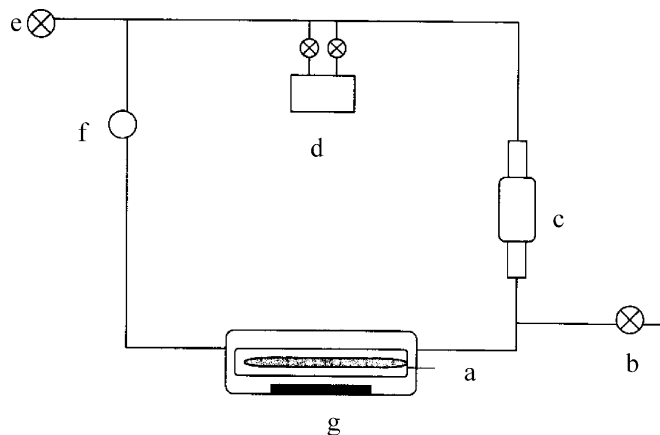


Fig. 1. Schematic diagram of a photocatalytic reactor: (a) 6 W black light; (b) evacuation pump; (c) circulation pump; (d) water cell; (e) leaking valve; (f) septum for sampling; and (g) TiO₂ film.

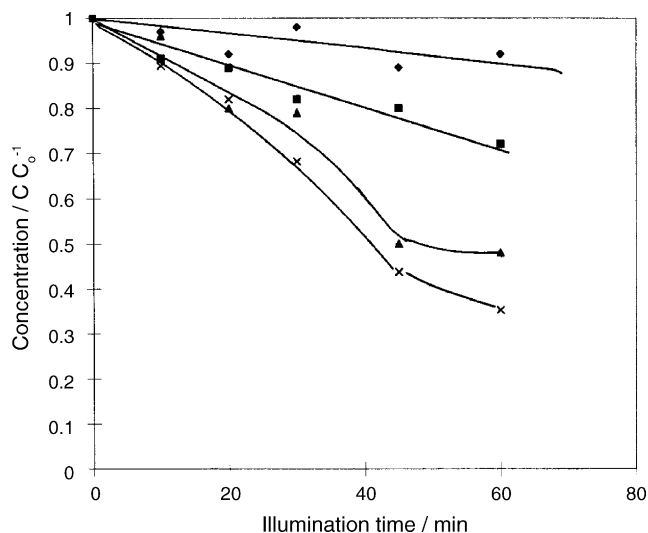


Fig. 2. Effect of PVP concentration on the degradation of ethylene. Spin-coated at 3000 rpm and calcined at 600 °C. PVP concentration: (■) 0% (5000 rpm); (▲) 20%; (×) 40%; (◆) absence of TiO₂.

as reported in several previous papers [19,20]. The large film thickness [21] may also be contributed to the improved activity, as it has been reported that the activity increases by repeated coating of thin film [19,22]. The effect of calcination temperature shown in Fig. 3 demonstrates that the optimum temperature is 600 °C in the presence of PVP. The dependence of the activity on calcination temperature may be related to the change in crystal structure of TiO₂. In X-ray diffraction pattern a small anatase peak was observed for the film calcined at 600 °C (20% PVP), whereas the peak was not detectable for one calcined at 650 °C. Previously one of the present authors reported that the photocatalytic activity of anatase TiO₂ prepared by sol-gel method increases with the calcination temperature and at 600–650 °C the anatase is transformed to less active rutile in the absence of PVP [23]. This previous observation suggests that a part of anatase is transformed to rutile in the film calcined at 650 °C. It

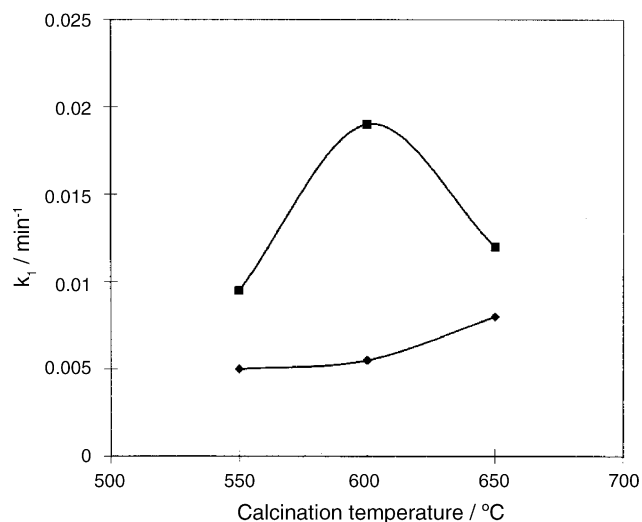


Fig. 3. Effect of calcination temperature on the degradation of ethylene (k_1 : first-order rate constant): PVP: (◆) 0% (5000 rpm of coating speed); (■) 40%.

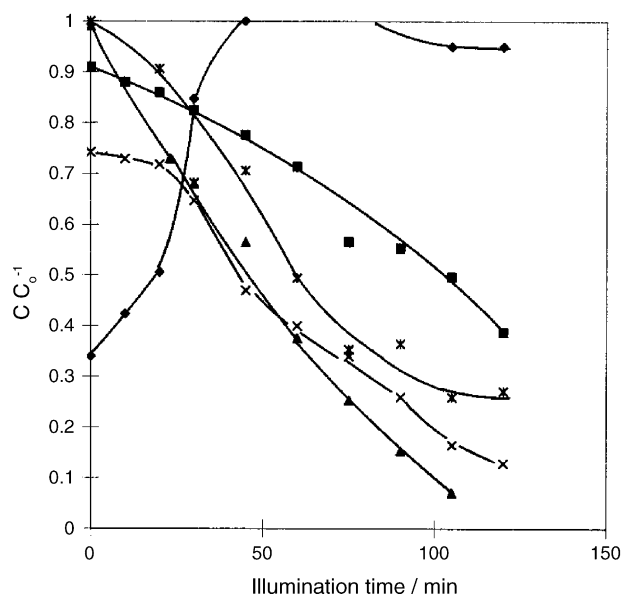


Fig. 4. Degradation of ethylene at different amounts of incorporated HSZ320 (40% PVP): (*) 0.0025; (×) 0.005; (▲) 0.01; (■) 0.02; (◆) 0.04 g/ml sol.

is also likely that the presence of PVP affects the crystallization process: the temperature of phase transformation shifts to higher temperature.

It was thus suggested that a set of conditions: 40% PVP; 3000 rpm of rotation speed; and 600 °C of calcination temperature, is optimum for good film quality and high photocatalytic activity. All the experiments afterward are based on the film prepared under these conditions. Some other characteristics of this film were reported in our previous paper [21].

3.2. Zeolite and silica-incorporated TiO₂ film

Two zeolite samples (HSZ320 and HSZ870) were employed to study the effect of Si/Al ratio of zeolite (Table 1). Fig. 4 demonstrates the effect of HSZ320 contents on the ethylene elimination. The activity (ethylene elimination rate) varied with zeolite content and the optimum was observed with 0.01 g zeolite/ml of coating sol (Fig. 5). With 0.04 g zeolite significant adsorption but nearly no degradation resulted. Ethylene concentration increased initially upon illumination of this film. Such unusual phenomenon may be explained by photodesorption. The loss of activity at high zeolite content can be attributed to the reduced TiO₂ ratio in the film and also the blocking of TiO₂ surface by zeolite from the incident light. The optimum content of zeolite is thus determined by a balance between the amount of adsorbed ethylene and the number of unblocked active sites. Different results were observed with HSZ870. Significant adsorption was noted for all the zeolite contents studied. For the initial 30–45 min of illumination the concentration of ethylene increased and then decreased. The optimum zeolite content was 0.005 g (Fig. 5). Comparing the two zeolite samples, the adsorption was larger with HSZ870 and the activity (evaluated by the time required for 90% ethylene elimination) was also slightly larger with HSZ870. This difference between the two zeolite samples can be attributed to their different Si/Al ratios. HSZ870

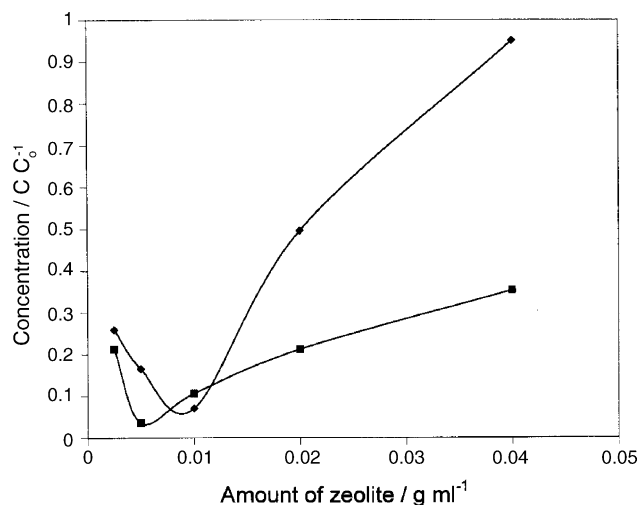


Fig. 5. Remaining ethylene ratio after 105 min illumination vs. amount of zeolite: (◆) HSZ320; (■) HSZ870.

with higher silica ratio has more hydrophobic surface and hence is favorable to ethylene adsorption. Since the importance of high silica content was suggested, the effect of silica powder instead of zeolite was studied. Two silica samples, OX50 and QS-09 from different manufacturers (Table 1), were used for this experiment. Large adsorption in the dark and subsequent desorption upon illumination was observed with OX50, whereas very little or no adsorption was shown with QS-09 (Fig. 6). Nevertheless the higher activity was noted with QS-09 than with OX50. This finding may indicate that the activity is not determined by the adsorption alone. In this regard it is suggestive that too strong adsorption suppresses the degradation [24]. For both silica samples the optimum content was 0.005–0.01 g/ml sol. The effects of different adsorbents (0.01 g/ml sol) were compared in Fig. 6. All the adsorbent-incorporated samples exhibited higher activ-

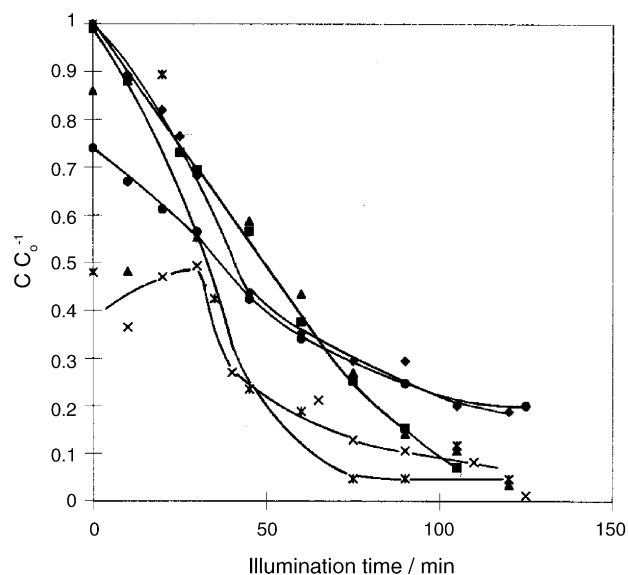


Fig. 6. Effects of different adsorbents (0.01 g/ml sol) on the degradation of ethylene: (◆) no adsorbent; (■) HSZ320; (▲) HSZ870; (×) OX-50; (*) QS-09; (●) TP-2.

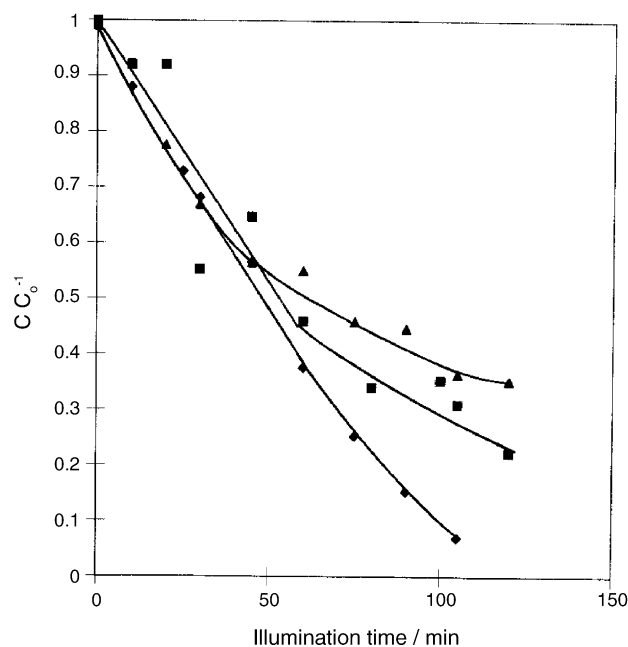


Fig. 7. Influence of humidity in the presence of HSZ320 (0.01 g/ml sol). Humidity: (▲) high; (■) dry; (◆) ambient.

ity than plain TiO₂ film. TiO₂ (TP-2) powder was also tested as an adsorbent. Nearly no activity increase resulted.

3.3. Influence of humidity

All the degradation experiments hitherto were carried out at ambient humidity. Considering zeolite and silica to be drying agents, humidity may affect the adsorption of ethylene. Influences of humidity at three levels, namely, high, low (dry) and ambient, were compared. The activity of HSZ320-incorporated film decreased either at high humidity or in dry air (Fig. 7). The similar but larger effect was observed with OX50-incorporated film. It appears that the influence of humidity is larger for the film of higher adsorption. These results demonstrated that the activity was highest at ambient humidity. The influence of humidity may be interpreted on the basis of water adsorption to the film. In TiO₂ photocatalysis water is essential to generate OH radical, a powerful oxidant, while it prevents ethylene from adsorbing to TiO₂ and adsorbent. These conflicting effects of water explain that the activity decreases either at high or low humidity, and is optimum around ambient humidity level where the two effects are balanced.

3.4. Intermediate identification

Three intermediates were identified: formic acid, formaldehyde and carbonate ion. The production yield of formic acid and formaldehyde from 2.1×10^{-3} mol/l ethylene on plain TiO₂ film after 4 h illumination were about 0.1 and 0.08 mol/mol of ethylene, respectively. Acetic acid, another possible stable intermediate, was not detected. In photocatalytic degradation of ethylene, the fission of C=C bond has been reported [25]. Our results support this mechanism. From these intermediates

detected the following possible degradation process was proposed: $C_2H_4 \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2$.

4. Conclusions

- (1) TiO_2 film of the best quality and highest activity was prepared from 40% PVP, 3000 rpm of spin coating speed and 600 °C of calcination temperature.
- (2) In zeolite- and silica-incorporated films the optimum adsorbent content was 0.005–0.01 g/ml of coating sol (0.042–0.085 g/g TiO_2).
- (3) Among five adsorbents incorporated, the highest activity was obtained with silica QS-09. Between the two zeolite samples one with lower Si/Al ratio exhibited better efficiency.
- (4) Humidity at high and low levels suppressed the activity.
- (5) Formaldehyde and formic acid were major intermediate compounds.

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