



## Photocatalytic degradation of benzene on zeolite-incorporated TiO<sub>2</sub> film

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### Abstract

Zeolite powder was incorporated into the TiO<sub>2</sub> film. Their photoactivities were evaluated for the gas phase degradation of benzene. Seven zeolite samples were used in this study and each enhanced the photocatalytic degradation. Humidity in the gas sample increased the degradation, but suppressed the adsorption of benzene to the TiO<sub>2</sub> film. It was noted that the photoactivity was inversely proportional to the silica/alumina ratio of zeolite, whereas adsorption increased with this ratio. It was suggested that the adsorption of water onto zeolite contributes to the enhancement of benzene degradation.

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### 1. Introduction

TiO<sub>2</sub> photocatalysis for the degradation of gaseous and aqueous pollutants has been studied extensively, and is already in practical use for some particular purposes such as disinfection and deodorization of air. However, its insufficient photoactivity limits its further application. Therefore, the enhancement of the photoactivity is of great concern from both practical and scientific viewpoints. Adsorbent incorporated in TiO<sub>2</sub> increases the photocatalytic activity by collecting pollutants to the photocatalyst surface from the air or solution [1–4]. Specifically, zeolite-supported TiO<sub>2</sub> was studied by several researchers [5–8].

The photocatalyst employed in these studies was in the form of powder: TiO<sub>2</sub> supported on zeolite particle. However, a film is more practical in most applications and study of such a film may provide different insight into the role of zeolite. In the present study,

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zeolite was incorporated in TiO<sub>2</sub> film prepared by sol–gel method, and factors affecting the photoactivity such as zeolite species, its amount and humidity in the sample gas were investigated.

## 2. Experiment

Seven zeolite samples used in this study were purchased from Tosoh Co. and used as supplied: HSZ 360, 320, 830, 860, 870, F-9 and A-4. Their silica/alumina ratio (cited from the product specification) and specific surface area (measured by Micromeritics FlowSorb 2300) are listed in Table 1. The TiO<sub>2</sub> film was prepared by the sol–gel method reported by Kato et al. [9]. General procedure for the preparation of zeolite-incorporated TiO<sub>2</sub> film is as follows. The mixture of 113.6 g titanium tetraisopropoxide, 42.4 g diethanolamine, 8.0 g polyethyleneglycol, 800 ml ethanol and 7.2 ml water was stirred magnetically for several minutes. Different amounts of zeolite crushed in a mortar was added to 3 ml of the above mixture, and vibrated by a supersonic vibrator. The suspension was left for 30 min. The coating procedure used is similar to a dip method: 0.25 ml of the supernatant solution was coated on both sides of a 150 mm × 20 mm Pyrex glass plate, and the plate was held vertically for several minutes for dripping. It was dried at 80 °C for 1 h, and then calcined in an electric oven. The temperature was raised at the rate of 12 °C/min to 550 °C and then kept for 1 h. The film was cleaned by vibrating in water and the surface was lightly smoothed with a cotton cloth.

The amounts of TiO<sub>2</sub> and zeolite in the supernatant solution was estimated by the following procedure. The solution was centrifuged and the zeolite separated dried and weighed. The amount of TiO<sub>2</sub> was estimated by heating the filtrate at 550 °C and weighing TiO<sub>2</sub> recovered. Approximate film thickness was measured by an optical micrograph.

A reactor for the photocatalytic degradation is similar to that illustrated in our previous paper [10]. The coated glass plate was placed in the reactor and benzene gas was circulated at the rate of 486 ml/min. Dried air was circulated before the humidity was adjusted.

A 6 W black light (Toshiba Litec Co.) was used to illuminate the glass plate. The wavelength of its maximum intensity is 350–360 nm. Sample gas was taken periodically by a syringe, and analyzed for remaining benzene by a Shimadzu GC 9A and for CO<sub>2</sub> by a Shimadzu GC 6A with a methanizer. CO<sub>2</sub> evolution rate was expressed by molecules per liter per hour for the amount formed during the initial 30 min. Adsorption of benzene to TiO<sub>2</sub>

Table 1  
Characteristics of zeolite

Zeolite (type)	Si/Al ratio	Specific surface area (m <sup>2</sup> /g)
HSZ 320 (Y) <sup>a</sup>	5.4	695
HSZ 360 (Y) <sup>a</sup>	13.7	672
HSZ 830 (ZSM-5) <sup>b</sup>	28	275
HSZ 860 (ZSM-5) <sup>b</sup>	68	191
HSZ 870 (ZSM-5) <sup>b</sup>	190	241
F-9 (X)	2.5	527
A-4 (A)	2	3.9

<sup>a</sup> H form.

<sup>b</sup> NH<sub>4</sub> form.

was estimated from the difference in benzene concentrations before and after the coated plate was placed, and expressed by percentage of added benzene. The film on a glass plate was scratched and the powder obtained was subjected to FTIR measurement by a Horiba FT 200. X-ray diffraction (XRD) was measured by a Rigakudenki RAX01.

### 3. Results and discussion

Three calcination temperatures, i.e. 500, 550 and 600 °C, for TiO<sub>2</sub> film containing HSZ 320 were tested. The highest activity was obtained at 550 °C. This trend is consistent with the result obtained in the absence of zeolite. To check the structure change of zeolite by calcination, XRD and FTIR were measured. There was no appreciable change in either XRD or FTIR of all zeolite samples before and after calcining at 550 °C. Following these results, the calcination temperature was fixed to 550 °C. The effect of zeolite (HSZ 320) amount on the photoactivity is shown in Fig. 1, in which zeolite amount was expressed by the amount added to ml of TiO<sub>2</sub> sol in the coated solution. Incorporation of zeolite did not change the XRD of the film. However, FTIR spectra in 600–900 cm<sup>-1</sup> region, which has been assigned to symmetric vibration of Si–O–Si [11,12], became broader in the film, suggesting the interaction between TiO<sub>2</sub> and silica. Bands for NH (1420, 1480 and 1680 cm<sup>-1</sup>) [13] were not observed for HSZ 860 and 870, whereas for HSZ 830, 1420 cm<sup>-1</sup> band was observed and diminished by calcining at 550 °C. Scanning electron micrograph observation showed a fairly good dispersion of zeolite particles. The film thickness was 3–4 μm for the most zeolites, but for HSZ 830, 870 and A-4 it was thinner (Table 1). It is assumed that some portion of zeolite is removed during washing and surface smoothing.

Disappearance of benzene and CO<sub>2</sub> formation were compared for the films prepared from 0.2 g zeolite and 3 ml TiO<sub>2</sub> sol under 50% relative humidity (Figs. 2 and 3). All the zeolite samples enhanced the degradation rate which was evaluated by benzene disappearance and CO<sub>2</sub> formation rates. But the photoactivity of the film varied greatly with zeolite. HSZ 320 and F-9 resulted in the largest enhancement of degradation rate. Fig. 3 also shows that a

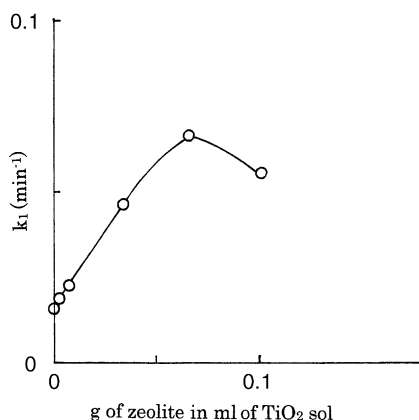


Fig. 1. Effect of zeolite (HSZ 320) content on benzene degradation.

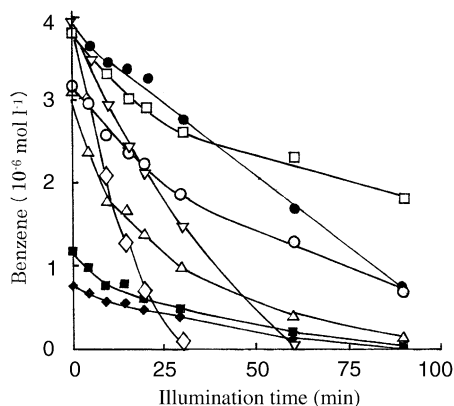


Fig. 2. Effect of zeolite on photocatalytic degradation of benzene (at 50% relative humidity). Control ( $\square$ ), HSZ 320 ( $\diamond$ ), HSZ 360 ( $\circ$ ), HSZ 830 ( $\triangle$ ), HSZ 860 ( $\blacksquare$ ), HSZ 870 ( $\blacklozenge$ ), F-9 ( $\nabla$ ), A-4 ( $\bullet$ ).

considerable portion of benzene is adsorbed to the film for HSZ 860 and 870. However, no obvious relation was noted between the photoactivity and the adsorption.

Humidity affected the photoactivity. Although it generally increased the activity, the effect of humidity varies with zeolite species (Fig. 4). In this experiment, films prepared by similar  $\text{TiO}_2$  and zeolite content sol were compared (Table 2). Humidity affected also the adsorption of benzene to the film: the adsorption decreased with the increase in humidity for HSZ 320 and 830, but only slightly for HSZ 860 and 870. The former group is a low silica/alumina ratio zeolite, while the latter is a high silica zeolite. These results suggest that for low silica zeolite, water competes favorably with benzene in the adsorption to zeolite and thus suppresses the degradation of benzene. However, water is also essential in photocatalysis as a source of OH radical. Accordingly, there is an optimal humidity for benzene degradation as observed typically in the case of HSZ 320 (Fig. 4). Whereas,

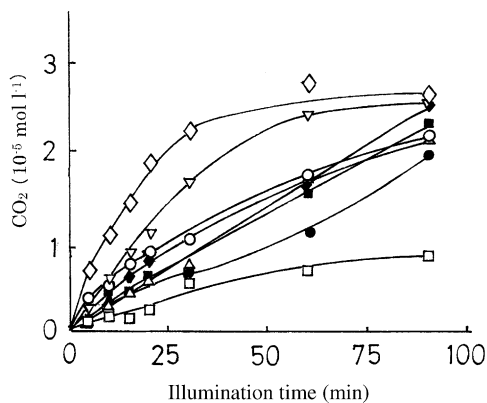


Fig. 3. Effect of zeolite on  $\text{CO}_2$  evolution in photocatalytic degradation of benzene (at 50% relative humidity). Symbols are the same as in Fig. 2.

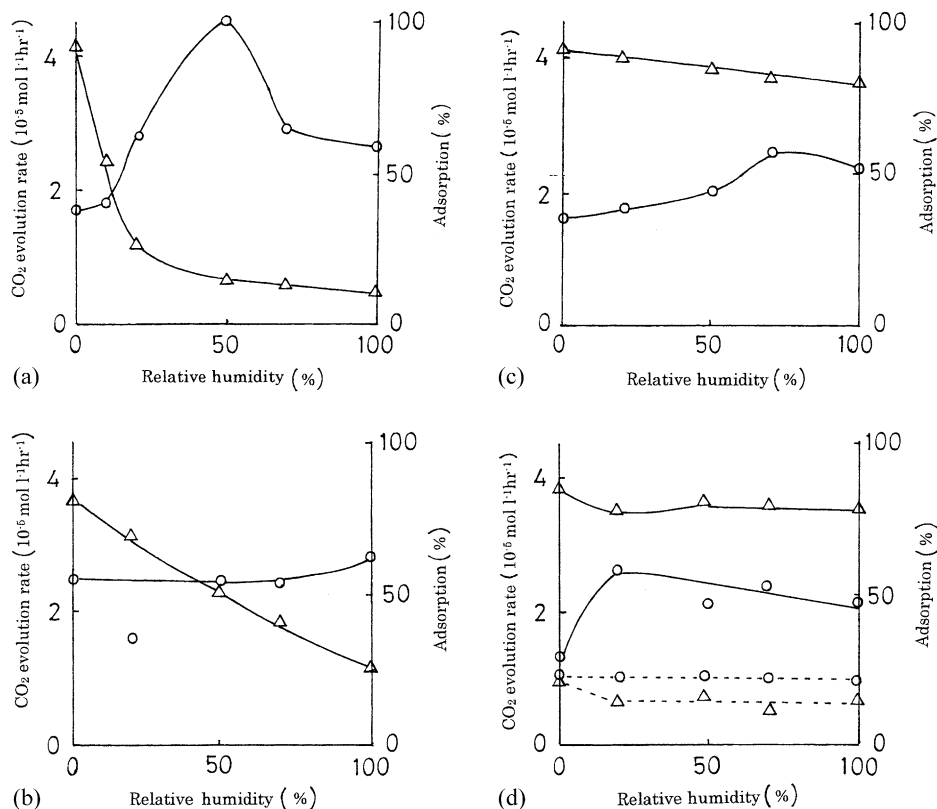


Fig. 4. Effect of humidity on CO<sub>2</sub> evolution and benzene adsorption: (a) HSZ 320, (b) HSZ 830, (c) HSZ 860, (d) HSZ 870. CO<sub>2</sub> evolution (○), adsorption (△), control (---).

for high silica zeolite such as HSZ 860 and 870 the adsorption of water is weak due to the hydrophobic nature of these zeolites [14,15], and it can not compete with benzene, resulting in only a slight effect of humidity both on benzene adsorption and degradation.

The silica/alumina ratio of zeolite was correlated with photoactivity of the film in Fig. 5. The photoactivity decreased with silica/alumina ratio of zeolite, consistent with the result

Table 2

Amounts of TiO<sub>2</sub> and zeolite in 3 ml of supernatant solution and average thickness of the coated layer

Zeolite sample	TiO <sub>2</sub> (mg)	Zeolite (mg)	Thickness of film (μm)
HSZ 320	5	10	4
HSZ 360	3	11	4–5
HSZ 830	4	13	2
HSZ 860	7	10	3
HSZ 870	6	10	2–3
F-9	4	9	3–4
A-4	6	9	2

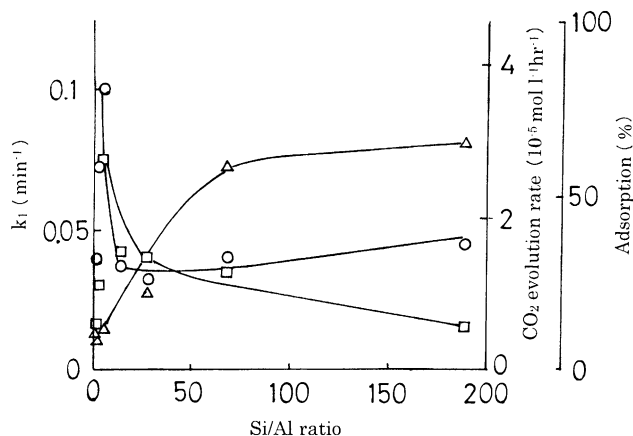


Fig. 5. Relation of Si/Al ratio of zeolite with benzene degradation and CO<sub>2</sub> evolution rates and benzene adsorption (at 50% relative humidity). CO<sub>2</sub> evolution (○), k<sub>1</sub> (□), adsorption (△).

for zeolite-supported TiO<sub>2</sub> suspension, while adsorption of benzene increased with this ratio. The very low activity of A-4 may be attributed to its low surface area (Table 2).

It is obvious from these results that the effect of zeolite is not attributed merely to the adsorption of benzene. In the literature the stabilization of reactive species such as OH radical and intermediate was suggested as a possible role of zeolite [16]. Considering that an adequate amount of water is important for photocatalysis (Fig. 4) and high alumina content of zeolite is favorable to adsorption of water, zeolite probably promotes the adsorption of water and hence increases the formation of OH radical [17]. In thermal catalysis on zeolite, silica/alumina ratio affects the reaction by altering the interaction between zeolite and adsorbed substance [18–20]. However, it is not likely in the present photocatalytic reaction that benzene adsorbed to zeolite is oxidized, because oxidizing agents such as OH radical generated on TiO<sub>2</sub> may not migrate from TiO<sub>2</sub> to adsorption site of zeolite [16]. It is more likely that benzene and water migrate from zeolite to active site of TiO<sub>2</sub>.

#### 4. Conclusions

1. Among seven zeolite samples studied the highest photocatalytic activity for the degradation of benzene was observed for HSZ 320.
2. Generally humidity increased the photoactivity.
3. Photoactivity was inversely proportional to silica/alumina ratio of zeolite.
4. The enhancement of photoactivity by zeolite can not be attributed only to the adsorption of benzene to zeolite. Water adsorption is also important.

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