J Wood Sci (2003) 49:79–85

ORIGINAL ARTICLE

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Photocatalytic activity of TiO_2 crystallite-activated carbon composites prepared in supercritical isopropanol for the decomposition of formaldehyde

Received: May 18, 2001 / Accepted: March 8, 2002

Abstract An effort was made to develop photocatalytic TiO_2 crystallite–activated carbon (TiO_2-AC) composites from tetraisopropyl titanate (TPT)-soaked activated carbon in supercritical isopropanol. It was subsequently found that TPT in supercritical isopropanol could be effectively converted to the anatase form of the TiO_2 crystallites. The prepared composites, composed of activated carbon as an adsorbent and the anatase form of TiO_2 as a photocatalyst, were evaluated for their adsorption capacity and subsequent photocatalytic activity against formaldehyde, one of the harmful air pollutants in the environment. As a result, the supercritically treated TiO_2–AC composites, particularly at 300°C and 350°C, had much higher formaldehyde-decomposing ability compared to a noncomposite comprising a simple mixture of activated carbon and TiO_2 granules. This indicates that the supercritical treatment can be effective for preparing the photocatalytic composites that have a high synergetic effect of adsorption and photocatalytic decomposition of formaldehyde for environmental cleaning.

Key words Formaldehyde · Supercritical treatment · Isopropanol · TiO_2 crystallite-activated carbon composites · Photocatalytic activity · Adsorptivity · Synergetic effect

Introduction

With the global expansion of environmental pollution, concentrations of toxic matters in the atmosphere and water have increased. For example, formaldehyde from wood adhesives used in the wooden construction materials for buildings and trihalomethane in water have proved to be harmful to humans.[1] It is therefore essential to remove the polluting substances, although such removal is often costly and inefficient.

As a good photocatalyst, titanium dioxide (TiO_2) is promising for environmental purification when irradiated with ultraviolet (UV) light because TiO_2 crystallites show strong oxidation and reduction abilities.[2] The photocatalyst effect of TiO_2 has recently been utilized in various fields of environmental purification, such as degradation of hazardous or malodorous compounds,[2] decolorization of dye wastewater,[3] direct decomposition of NO_x or SO_x, and purification of air and water.[4]

Some research on the photocatalytic activities of TiO_2 crystallite–activated carbon (TiO_2-AC) composites has been reported in which the adsorbed compounds were successfully transported to sites on TiO_2 gel, and photocatalytic effects were achieved.[5,6] Doi et al.[7] have prepared various types of TiO_2-wood inorganic composites, which were converted to carbonized wood–TiO_2 composites by thermal carbonization. These composites were composed of wood charcoal as an adsorbent and the anatase form of TiO_2 as a photocatalyst. It was then found that the highest synergetic effect on formaldehyde adsorption and subsequent photocatalytic activity existed when TiO_2 crystallites were deposited in the wood cell lumens and the surfaces of the charcoal particles. The appearance of the synergetic effect was thus concluded to be closely related to the distribution of the TiO_2 crystallites. In addition, it became clear that the decomposition of formaldehyde by photocatalytic activity progresses effectively in the presence of water because of the strong oxidizing power of hydroxy radicals from that water.[8]

On the other hand, supercritical treatment of isopropanol was recently reported to be effective for synthesizing TiO_2.[9,10] If activated carbon as a starting material can be compounded with TiO_2 granules by supercritical treatment, a high synergetic effect of the adsorption and photocatalytic activity can be expected. In this study, therefore, we applied supercritical treatment of isopropanol to prepare TiO_2-AC composites through the sol-gel reaction of titanium alkoxide in isopropanol. The prepared composites were

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then studied for their adsorption behavior and photocatalytic activity against formaldehyde (an example of an air pollutant) to evaluate the potential of supercritical treatment for their preparation.

Materials and methods

Supercritical treatment

Supercritical treatment was carried out by a batch-type reaction system, where a 5-ml reaction vessel made of inconel-625 was fully charged with reactant and solvent.[11] To start the supercritical treatment, the reaction vessel was quickly heated by immersing it in a molten tin bath preheated to a designated temperature (250°–450°C) and maintained for 1 min. To stop the reaction, the reaction vessel was placed in a waterbath for cooling. During the treatment the temperature and pressure of the reaction vessel were monitored by a thermocouple and pressure gauge, respectively, installed in the reaction vessel.

Table 1 shows the maximum temperature and maximum pressure in the reaction vessel under various conditions. The maximum pressures in the reaction vessel are all above a critical pressure of isopropanol (P_c 5.37 MPa), and the maximum temperatures in the reaction vessel are above the critical temperature of isopropanol (T_c 235°C) except for 250°C in the tin bath. Therefore, the supercritical conditions of isopropanol could be achieved at tin bath temperatures of 300°–450°C, whereas at 250°C the subcritical condition of isopropanol resulted.

Preparation of samples

Tetraisopropyl titanate (TPT; 1 g) was added to 4 ml isopropanol in a 5-ml reaction vessel, and the mixture was treated by ultrasonification. It was then treated at designated temperatures and times.

To prepare the TiO_2-AC composites in supercritical isopropanol, the activated carbon (0.2 g) (activated charcoal powder from wood sawdust washed with hydrochloric acid; Extra Pure Reagent, Nacalai Tesque) was added to tetraisopropyl titanate (4 g) in 15 ml of isopropanol. The mixture was treated by ultrasonification and then decanted to remove the supernatant. Subsequently, the soaked activated carbon was treated in air for the sol-gel reaction[7,12] for a few hours to obtain TiO_2-AC composites. These composites were then treated with supercritical isopropanol to obtain supercritically treated TiO_2-AC composite (Sc-TiO_2-AC) and subcritically treated TiO_2-AC composite (sub-TiO_2-AC). We also examined the synergetic effect for a simple mixture of supercritically treated TiO_2 (Sc-TiO_2) granules with activated carbon.

Characterizations of samples

To examine the distributions of TiO_2 granules in the TiO_2-AC composites, samples were observed by the JEOL scanning electron microscope (JSM-T330A) at an accelerating voltage of 10 keV. To determine the constituents of the TiO_2-AC composites, about 15 mg of the sample was heated in a thermogravimetric (TG) analyzer (TGA; Shimadzu TA-50) up to 950°C at a heating rate of 20°C/min under airflow (50 ml/min), whereupon all organic residues were burned out. The contents of TiO_2 gel and activated carbon were then determined according to the method by Doi et al.[7] from the following equations.

$$TiO_2 \text{ content } (\%) = W_T/W_{T+W} \times 100 \quad (1)$$

$$\text{Activated carbon content } (\%) = 100 - TiO_2 \text{ content} \quad (2)$$

where W_T is the weight of the TiO_2 granules without any organic residues, and W_{T+W} is the oven-dried weight of the sample at 170°C.

Based on the contents of the TiO_2 granules and the activated carbon obtained by Eqs. (1) and (2), the constituents of the samples could be determined as in Table 2. Note that the higher the supercritical treatment temperature, the higher the TiO_2 granule content. The amount of each sample tested was normalized to contain 10 mg of TiO_2 granules.

X-ray diffractograms were obtained by RINT2000 (Rigaku Denki) to examine the crystallographic structures of the TiO_2 granules under Cu-K_α radiation (λ = 0.1542 nm) using a K_β filter, operated at 40 keV and 30 mA, integrating five times. The average crystallite size of the anatase-form TiO_2 granules was calculated by Scherrer's equation.

$$\text{Average crystallite size} = K \cdot \lambda/\beta \cdot \cos\theta \quad (3)$$

where λ is the radiation wavelength (Å), β is the integral width of the peak at $2\theta = 25.3$ (degrees), θ is Bragg's angle in the [101] plane, and K is Scherrer's value (0.94).

Table 1. Supercritical and subcritical conditions of isopropanol at various temperatures and pressures

Temperature of tin bath (°C)	Reaction vessel parameters		Condition achieved
	Temperature (°C)	Pressure (MPa)	
250	225	8	Subcritical
300	295	12	Supercritical
350	345	16	Supercritical
400	395	20	Supercritical
450	445	23	Supercritical

Table 2. Constituents of samples studied and the amounts of samples tested for adsorption and photocatalytic activities

Sample	Content (%)		Amount of sample tested (mg)[a]
	TiO_2	Activated carbon	
AC	0	100	15.0
Sc-TiO_2	100	0	10.0
Mixture of the above	40	60	25.0
Sub-TiO_2-AC (250°C)	19.8	80.2	50.5
Sc-TiO_2-AC			
300°C	27.9	72.1	35.8
350°C	45.4	54.6	22.0
400°C	50.5	49.5	19.8
450°C	63.6	36.4	15.7

[a] Amount normalized to contain 10 mg of TiO_2 except for activated carbon, for which an arbitrary weight of 15 mg was used

To evaluate the adsorption capacity and various surface areas, 30–40 mg of each sample, dried and degassed, was subjected to a nitrogen adsorption measurement. The drying and degassing were carried out with a heating device (Shimadzu, Flow Prep 060) in nitrogen at 105°C for 2 h and at 400°C for 1 h, respectively. During the subsequent adsorption of nitrogen, isotherms at 77 K (−196°C) were measured to determine the internal surface area [including macropores (>500 Å in diameter), mesopores (500–20 Å), and micropores (20–8 Å)], the external surface area, and the Brunauer-Emmett-Teller (BET) area[13] by the t-plot method using micromeritics (Shimadzu, Gemini 2375).

Evaluation of photocatalytic activities

A previously developed apparatus was used to examine the combined performance of the adsorption capacity and the photocatalytic activity for TiO_2-loaded samples. In the test of such a synergetic effect to be conducted under irradiation with UV light, formaldehyde was selected as a model harmful air pollutant.[7]

An oven-dried sample of a designated amount (Table 2) was dispersed in ethanol and then spread over the glass surface of a petri dish 58 cm^2 in area for 30–60 min at 105°C and cooled to room temperature in a desiccator. The sample was then pretreated under UV light irradiation in the evaluation apparatus filled with pseudo-air until carbon dioxide evolution stopped.

After the UV light was cut off, the gas inside the apparatus was substituted with 1.8 l gas composed of formaldehyde (about 400 ppm) in pseudo-air. This gas was then circulated inside the apparatus at a flow rate of 3.6 l/min and a temperature of 23°–26°C. The treatment time was measured from the point at which the circulation started. During the treatment UV light was irradiated from a Black Lamp (Toshiba FL 6BL). For all samples, the light intensity in the reaction vessel was 0.49–0.50 mW/cm^2 at a wavelength of 365 nm. The concentrations of formaldehyde and its decomposed products were measured from the peak area of the chromatograms obtained by gas chromatography-mass spectiometing (GC-MS) (Shimadzu QP-5000A) by time-lag gas sampling.

To examine the adsorption behavior, the UV light was turned off for a certain time until the adsorption of formaldehyde was observed. The UV light was then turned on to irradiate the samples.

The relative decomposition rate (RDR) of the formaldehyde gas was calculated from

$$\mathrm{RDR} = A_{200} / A_{200\mathrm{max}} \quad (4)$$

where A_{200} is an incremental area in the GC-MS chromatogram of CO_2 under UV light irradiation for 200 min, and $A_{200\mathrm{max}}$ is the maximum value among all the samples studied, as described previously.[7]

Results and discussion

X-ray diffractometry

The X-ray diffractograms of the samples studied are shown in Fig. 1. It is evident that the activated carbon and TiO_2-AC composites without supercritical treatment are amorphous, and that the TiO_2 gel in the composite treated at 250°C (sub-TiO_2-AC) is slightly crystallized. However, at temperatures above 300°C, the TiO_2 gel in the composites was converted to the anatase form of crystallites; and at higher treating temperatures, the degree of TiO_2 crystallinity was higher. Therefore, supercritical treatment in isopropanol ($>T_c$ 234.9°C; $>P_c$ 5.37 MPa) is effective for preparing the anatase form of TiO_2-AC composites.

Although it is not clear in Fig. 1, closer inspection of the X-ray diffractograms indicated that the TiO_2 crystallites are larger (about 15.8 nm) in the composites prepared at 450° and 400°C than those prepared at 350° and 300°C (13.5 nm).

Scanning electron microscopic observations

Figure 2 shows scanning electron microscopy (SEM) micrographs of TiO_2-AC composites prepared at various supercritical and subcritical conditions of isopropanol with treatment for 1 min. It is apparent that the TiO_2 granules are fixed on the surface of the activated carbon. In addition, as

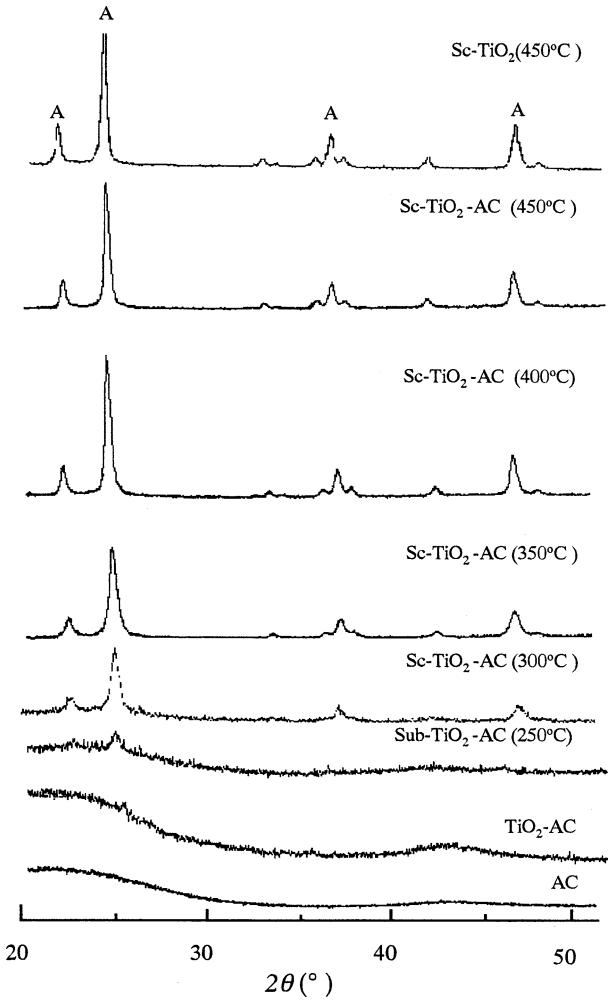

Fig. 1. X-ray diffractograms of supercritically treated TiO_2-activated carbon (*Sc-TiO$_2$-AC*) and subcritically treated TiO_2-AC (*sub-TiO$_2$-AC*) composites prepared at various supercritical and subcritical conditions of isopropanol for 1 min. Those of Sc-TiO_2, TiO_2-AC, and AC were included for comparison. *A*, anatase-type crystallite

the supercritical treatment temperature rose, increasing numbers of TiO_2 granules were fixed on the surface of the activated carbon. These results are in good agreement with those in Table 2 after thermogravimetric analysis of samples.

Evaluation of adsorption capacity and special surface area

The two important factors for the adsorbent and photocatalyst are the surface area and internal surface structure, which are dependent on the preparation methods of samples. The adsorption capacity and the surface area are thus important if the sample is to behave effectively during adsorption and the subsequent photocatalytic reaction. The adsorption capacity based on nitrogen adsorption and surface area were therefore measured by nitrogen adsorption isotherms.

The external surface area, BET specific surface area, and internal surface area were determined at the same time. Table 3 shows the results, which indicate that the adsorption capacity and surface area of the sub-TiO_2-AC and Sc-TiO_2-AC composites are much higher than those of the Sc-TiO_2 granules. Among these composites, those treated at 400°C have the highest values, and those treated at 450°C have the lowest, perhaps owing to destruction of the internal surface structure of the samples at the higher temperature. Although the values for the Sc-TiO_2-AC composites are not as high as those for activated carbon alone, they can be expected to have the potential to adsorb air pollutants.

Evaluation of photocatalytic activity

Noncomposites

Figures 3 and 4 show the changes in formaldehyde and CO_2 concentrations for activated carbon and Sc-TiO_2 granules, respectively, as evaluated before and after UV light irradiation. It is apparent from Fig. 3 that formaldehyde sharply

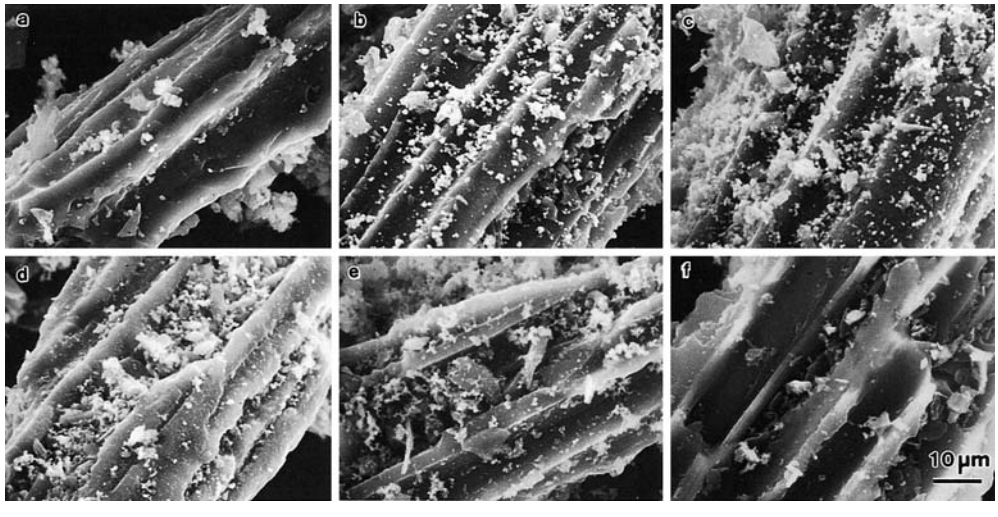

Fig. 2. Scanning electron microscopy (SEM) micrographs of Sc-TiO_2-AC and sub-TiO_2-AC composites prepared at various supercritical and subcritical conditions of isopropanol for 1 min. **a** 250°C. **b** 300°C. **c** 350°C. **d** 400°C. **e** 450°C. **f** Micrograph of AC is included for comparison. *Bar* **a–f**, 10 μm

Table 3. Comparisons of adsorption capacity and surface area of the samples studied

Sample	Adsorption[a] (m^3/g)	Surface area (m^2/g)		
		Internal	External	BET
AC	325	805	735	962
Sc-TiO_2	3	9	5	9
Sub-TiO_2-AC (250°C)	117	277	271	344
Sc-TiO_2-AC				
300°C	111	276	240	325
350°C	125	296	300	370
400°C	156	408	338	463
450°C	77	205	177	232

BET, Brunauer-Emmett-Teller
[a] By nitrogen adsorption

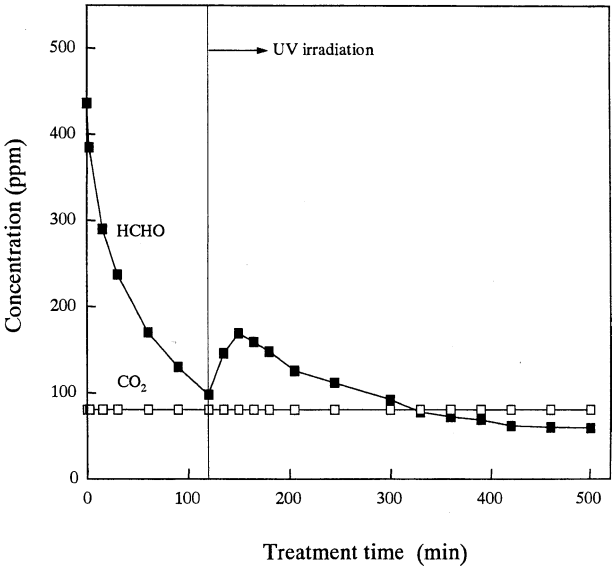

Fig. 3. Changes in formaldehyde (*HCHO*) and carbon dioxide (CO_2) concentrations depending on the treatment time before and after ultraviolet (*UV*) irradiation of AC

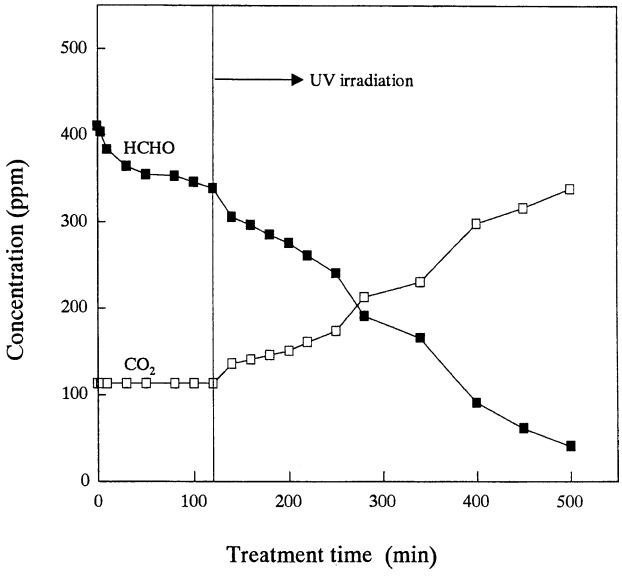

Fig. 4. Changes in HCHO and CO_2 concentrations depending on the treatment time before and after UV irradiation of Sc-TiO_2 granules

decreases during the early stage of treatment by the activated carbon. After UV light irradiation, however, the formaldehyde concentration is somewhat increased but gradually decreases again, owing perhaps to desorption of the adsorbed formaldehyde gas from the activated carbon by the temperature rise due to UV light irradiation. This phenomenon was not observed in a previous study with wood charcoal prepared by thermal carbonization.[7] In contrast to such a change in formaldehyde concentration, the CO_2 concentration remained unchanged regardless of UV light irradiation. Thus, activated carbon cannot decompose formaldehyde.

On the other hand, the anatase-form Sc-TiO_2 crystallite granules shown in Fig. 4 can adsorb formaldehyde only slightly before UV light irradiation. During this period the CO_2 concentration remained constant; therefore, the gradual decrease in formaldehyde concentration must be due to its adsorption. After UV light irradiation, however, the CO_2 concentration was increased. Thus, adsorbed formaldehyde would be decomposed to CO_2 by the photocatalytic activity of the TiO_2 crystallites. Despite its photocatalytic capacity, the adsorption rate of formaldehyde is much smaller for the Sc-TiO_2 granules than for the activated carbon in Fig. 3.

Figure 5 shows the results for the simple mixture of Sc-TiO_2 granules and activated carbon. The strong adsorption behavior (derived mainly from the activated carbon) and photocatalytic decomposition (by the TiO_2 granules) can be seen. However, a synergetic effect of the adsorption and subsequent photocatalytic decomposition is not apparent, a point that can be proved by desorption of formaldehyde after UV light irradiation due to the high energy of the UV light. This behavior indicates that even though a high concentration of formaldehyde is adsorbed onto the activated carbon it is not close enough to TiO_2 crystallites to be photocatalytically decomposed effectively by the TiO_2.[7]

TiO_2-AC composites prepared by subcritical and supercritical treatments

Figure 6 shows the changes in formaldehyde and CO_2 concentrations for sub-TiO_2-AC composites prepared at 250°C

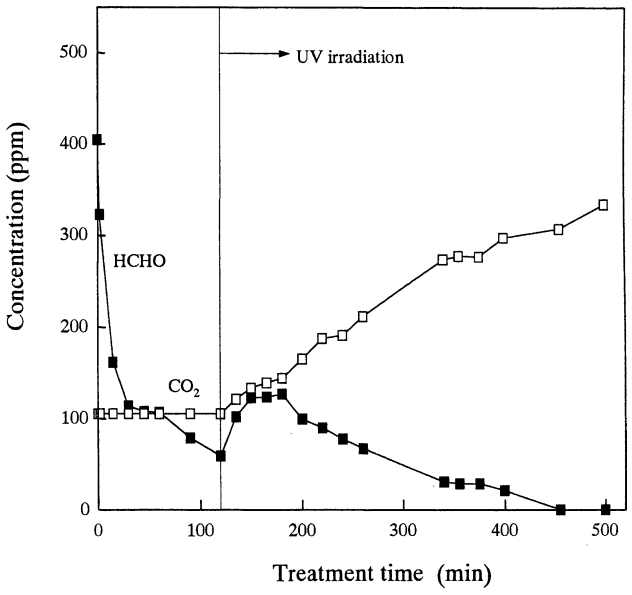

Fig. 5. Changes in HCHO and CO_2 concentrations depending on the treatment time before and after UV irradiation of a simple mixture of AC and Sc-TiO_2 granules

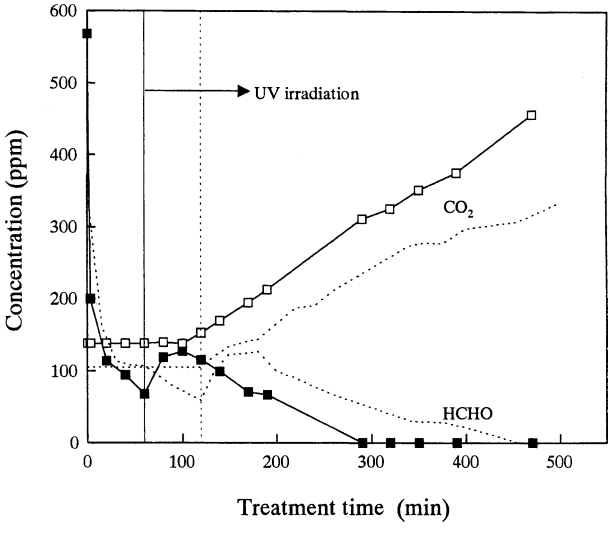

Fig. 6. Changes in HCHO and CO_2 concentrations depending on the treatment time before and after UV irradiation of the sub-TiO_2-AC composite prepared at a tin bath temperature of 250°C for 1 min. Results for the simple mixture of AC and Sc-TiO_2 granules in Fig. 5 are included for comparison (*dotted lines*)

for 1 min. As shown in Fig. 1, the TiO_2 granules in this composite have an amorphous nature with only slight crystallinity. In addition, the trend seen in Fig. 6 is similar to that in Fig. 5, as shown by the dotted line, where the desorption of formaldehyde was observed without any synergetic effect of the adsorption or the photocatalytic activity after UV light irradiation.

Figure 7, however, shows a different result for the Sc-TiO_2-AC composites prepared at 350°C for 1 min. The formaldehyde concentration is obviously decreased at an early stage. After UV light irradiation, however, desorption of formaldehyde gas is not apparent, as observed in Fig. 6. Instead, the CO_2 concentration increases rapidly, and formaldehyde is completely decomposed to CO_2. For comparison, results for the simple mixture of activated carbon and Sc-TiO_2 granules (Fig. 5) are included (dotted lines). Therefore, a synergetic effect in the Sc-TiO_2-AC composites must exist for adsorption and subsequent photocatalytic activity. As a result, Sc-TiO_2-AC composites prepared by supercritical isopropanol at 350°C for 1 min render themselves more active for decomposing formaldehyde.

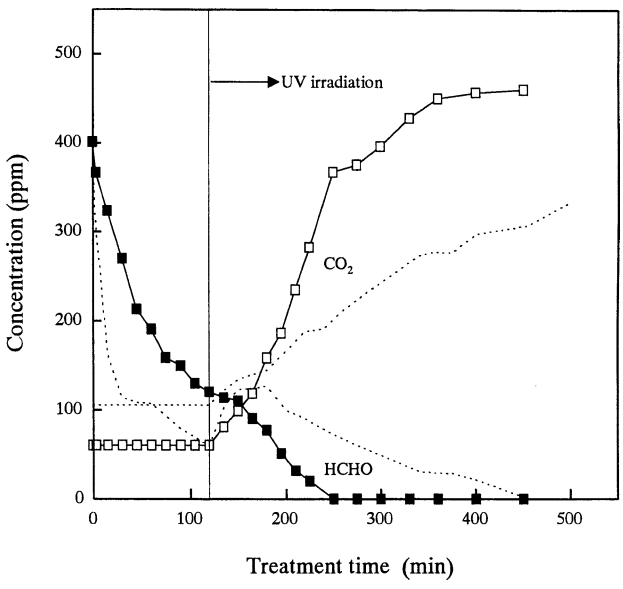

Fig. 7. Changes in HCHO and CO_2 concentrations depending on the treatment time before and after UV irradiation of an Sc-TiO_2-AC composite prepared at a tin bath temperature of 350°C for 1 min. Results for the simple mixture of AC and Sc-TiO_2 granules in Fig. 5 are included for comparison (*dotted lines*)

Table 4. Relative decomposition rates of the samples studied

Sample	RDR[a]
AC	0
Sc-TiO_2	0.2
Mixture of the above	0.2
Sub-TiO_2-AC (250°C)	0.2
Sc-TiO_2-AC	
300°C	1.0
350°C	0.9
400°C	0.6
450°C	0.5

RDR, relative decomposition rate
[a] Values are relative to Sc-TiO_2-AC (300°C)

Table 4 shows the relative decomposition rates (RDRs) for formaldehyde in this experiment. It is clear that the Sc-TiO_2-AC composites prepared at 300°, 350°, 400°, and 450°C have much larger RDRs, than the sub-TiO_2-AC composites prepared at 250°C or a simple mixture of Sc-TiO_2 and activated carbon. This indicates that the supercritical treatment, particularly at 300° and 350°C, can be most effective for preparing the photocatalytic TiO_2-AC composites

that have a high synergetic effect of adsorption and photocatalytic decomposition of formaldehyde.

The lower effect observed for the Sc-TiO_2-AC composites prepared at 450°C would be due to destruction of the micropore structure of the samples, as shown in Table 3. Although the composites prepared at 400°C have the highest adsorption capacity, as in Table 3, the overall decomposition ability was not as high as expected (Table 4). The reason for this result is not known. However, the particle sizes of the TiO_2 crystallites are larger in the composites prepared at 400° and 450°C than in those prepared at 300° and 350°C, as mentioned earlier. The smaller particles are reported to have higher photocatalytic activity.[14] This is likely to be one reason for the observed lower decomposition rate for samples treated at 400°C.

Conclusions

It was found that the sol-gel reaction of tetraisopropyl titanate (TPT) in supercritical isopropanol can be highly effective for its conversion to the anatase form of TiO_2 crystallite structure. The supercritically prepared TiO_2-AC composites were found to adsorb and decompose formaldehyde photocatalytically to CO_2, with a much higher synergetic effect than a simple mixture of TiO_2 and activated carbon. The supercritical treatment of TPT in isopropanol with activated carbon is therefore a simple, powerful method for preparing photocatalytic TiO_2-AC composites. Further research will be aimed at understanding the optimal processes and conditions of supercritical treatment to increase the adsorption and subsequent photocatalytic activity of the TiO_2-AC composites.

Acknowledgments The authors express their sincere thanks to Miss H. Tokoro and Mr. D. Kusdiana for their kind, valuable help and cooperation and to Dr. H. Miyafuji for SEM observations of samples, all at the Graduate School of Energy Science, Kyoto University.

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