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Supercritically treated TiO_2 -activated carbon composites for cleaning ammonia

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Abstract Supercritically treated TiO_2 -activated carbon (Sc-TiO₂-AC) composites were studied for their adsorption and photocatalytic activities toward gaseous ammonia (NH₃). The experiments were carried out at 26°C using a black lamp. The Sc-TiO₂-AC composites attained higher photocatalytic activities than supercritically treated TiO₂ (Sc-TiO₂). NH₃ was found out to be converted by the Sc-TiO₂-AC composites to compounds such as N₂, N₂O, NO₂⁻, and NO₃⁻. The main product was harmless N₂. The Sc-TiO₂-AC composites are expected to be applied as effective cleaning materials to environments that emit offensive NH₃ odors.

Key words Supercritical treatment \cdot TiO₂ \cdot Activated carbon \cdot Ammonia \cdot Decomposition mechanism

Introduction

Gaseous ammonia (NH₃) emitted from cigarettes, excreta, and kitchen garbage, among other things, is toxic and corrosive to some materials, and has a pungent odor. Exposure to high levels of ammonia can cause irritation and serious burns to the skin, mouth, throat, lungs, and eyes, especially for people with asthma. Therefore, the removal of NH₃ from gaseous or liquid waste streams is becoming an increasingly important issue. Traditional methods for the removal of NH₃ include biological treatment,¹ deepwell injection,² adsorption,³ and thermal incineration.⁴ Many studies on the removal of NH₃ have involved hightemperature catalytic oxidation of NH₃ using a variety of solid catalysts such as metals and oxides.⁵⁻⁷ However, relatively little work has been published on the photocatalytic oxidation of NH₃ using TiO₂ under ultraviolet (UV) irradiation. Bonsen et al.⁸ studied the decomposition of NH₃ by UV irradiation in water with TiO_2 as photocatalyst. Wang et al.⁹ found that degradation of NH_3 was possible with irondoped TiO_2 as a photocatalyst in acidic solution. Little study on gaseous NH_3 decomposition has been performed. Nazir et al.¹⁰ studied photocatalytic degradation of gaseous NH_3 on TiO_2 that was deposited on carbon particles. Mozzanega et al.¹¹ reported NH_3 decomposition over TiO_2 at room temperature, using a flow-type evaluation system for photocatalytic activity of TiO_2 that was applied in other studies.^{12,13}

On the other hand, it is known that wood charcoal or activated carbon is effective for the removal of harmful substances in the environment by their excellent adsorption characteristics. Therefore, taking into account that photocatalytic activity of TiO₂ has a direct relation with its adsorption ability for pollutants, research on photocatalytic activities of TiO₂ with wood charcoal or activated carbon has been reported, in which the synergetic effects of adsorption and photocatalysis were observed. Torimoto et al.¹⁴ studied photodegradation behaviors of dichloromethane on TiO₂-loaded activated carbon. Nozawa et al.¹⁵ developed a deodorization system using TiO₂ supported on activated carbon fibers. Furthermore, in our laboratory, TiO₂-carbon composites that were composed of carbon as an adsorbent and the anatase-form of TiO₂ crystallite as a photocatalyst have been developed.¹⁶⁻¹⁸ Doi et al.¹⁶ studied the decomposition of formaldehyde with carbonized wood-TiO2 composites, and found that the prepared composites have the synergetic effects of adsorption and photocatalytic activity, compared with TiO₂ itself or the mixture of the carbonized wood and TiO₂. It was also revealed that water has an important role in the decomposition of formaldehyde with these composites.¹⁷ In the meantime, it has been found that the composites can retain their effective performance and be used for long periods with little attention. Huang and Saka¹⁸ developed supercritically treated TiO₂-activated carbon composites that have higher adsorption and photocatalytic activities for formaldehyde than TiO₂ or the mixture of activated carbon and TiO₂.

In this study, supercritically treated TiO_2 -activated carbon (Sc-TiO₂-AC) composites were studied for their

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adsorption of and photocatalytic activities on gaseous NH_3 . A decomposition mechanism of NH_3 was also studied by determining the intermediates and end-products of NH_3 decomposition.

Materials and methods

Preparation of samples

Activated carbon (0.2g) (AC; activated charcoal powder from wood sawdust washed with hydrochloric acid, Extra Pure Reagent; Nacalai Tesque) was added to the solution of tetraisopropyl titanate (TPT) (4g) in 15 ml of isopropanol. The mixture was then treated by ultrasonification for 30 min, and decanted to remove the supernatant. Subsequently, the TPT-soaked AC was treated in air for the sol-gel reaction for 5 h to obtain TiO₂–AC composites. The TiO₂–AC composites were then treated with supercritical isopropanol at 300°C and 12 MPa, which were above the critical temperature ($T_c = 235^{\circ}$ C) and pressure ($P_c =$ 5.37 MPa) of isopropanol, for 5 min to obtain supercritically treated TiO₂–AC composites (Sc-TiO₂-AC).

Supercritical treatment was carried out by a batch-type reaction system described elsewhere, where a 5-ml reaction vessel made of Inconel-625 was fully charged with reactant and solvent.¹⁹

Characterization of samples

To study the constituents of the Sc-TiO₂-AC composites, about 20 mg of the sample was heated in thermogravimetric analyzer (TGA, TA-50; Shimadzu) up to 900°C with a heating rate of 20°C/min under air flow (50 ml/min) whereupon all organic residues were burnt out. The content of TiO₂ gel and AC were then obtained, according to the method of Doi et al.,¹⁶ from the following equations:

 $\mathrm{TiO}_{2} \operatorname{content} (\%) = W_{T} / W_{\mathrm{T+W}} \times 100$ (1)

$$AC (\%) = 100 - (TiO_2 \text{ content})$$
(2)

where $W_{\rm T}$ is the weight of the TiO₂ granules without any organic residue, and $W_{\rm T+W}$ is the over-dried weight of the sample at 170°C.

Based on the content of TiO_2 granules and AC from Eqs. 1 and 2, the Sc- TiO_2 -AC composites contained the same weight of TiO_2 as that of Sc- TiO_2 used in the preparation.

X-ray diffractograms were obtained (RINT2000; Rigaku Denki) to examine the crystallographic structures of TiO₂ granules under Cu-K α radiation ($\lambda = 0.1542$ nm) using a K_{β} filter, operated at 40 keV and 30 mA, integrating five times.

Evaluation of adsorption and photocatalytic activities

To evaluate the adsorption and photocatalytic activities of the Sc-TiO₂-AC composites on NH_3 , a previously developed evaluation apparatus was used.¹⁶ An oven-dried

sample (containing 10 mg of TiO_2) was dispersed in ethanol and then spread over the glass surface of a petri dish (58 cm^2 in area) for 30 min at 105° C and cooled to room temperature in a desiccator. The sample was then pretreated under UV irradiation in the evaluation apparatus filled with helium (purity 99.999%).

After the UV light was cut off, the gas inside the apparatus was substituted with 1.81 of gas that was composed of He and O_2 gases in a volume ratio of 4:1, was humidified with H_2O at 25°C to be 50% in relative humidity, and had an NH₃ concentration of 2500 ppm. To distinguish atmospheric N_2 (¹⁴N: 99.37%, ¹⁵N: 0.37% in the air) from the N₂ produced by photocatalytic reaction of NH₃ with TiO₂, isotopic ¹⁵NH₃ (Taiyo) was used instead of environmental ¹⁴NH₃. The gas was then circulated inside the apparatus at a flow rate of 3.61/min and a temperature of 26°C. The treatment time was measured from when the circulation started.

The UV light was turned off for the first 100min in treatment time to examine adsorption behavior and then turned on to irradiate the sample. The light used for UV irradiation was from a black lamp (FL 6BL; Toshiba). For all samples, the light intensity in the reaction vessel was 0.49–0.50 mW/cm² at a wavelength of 365 nm.

The sampling gas was analyzed by gas chromatography (GC-14B; Shimadzu) with a column of Chromsorb103 (80/100 mesh) for ¹⁵NH₃, and Porapak Q 80/100 connected with Porapak R 80/100 for ¹⁵N₂O. For quantification of ¹⁵N₂, the sampling gas was also analyzed by gas chromatographymass spectrometry (GC-MS, QP-5000A; Shimadzu) with a column of CP-Poraplot Q. The column temperature was held at 70°C for GC and at 25°C for GC-MS, respectively. Helium was used as carrier gas at a flow rate of 40 ml/min.

For detection of ¹⁵NO and ¹⁵NO₂, the sampling gas was analyzed during the photocatalytic process using nitrogen oxides detector tubes (IM0010J2; Gastec). To determine the compounds maintained on the samples, samples treated for 600min were taken from the reactor and extracted with ultrapure water (7 ml). Subsequently, the resulting aqueous solution was analyzed by capillary electrophoresis (CE, HP3D CE system; Agilent). For quantification of ${}^{15}NO_{2}^{-}$ and $^{15}NO_{3}$, the fused silica capillary (50 μ m in inner diameter, 112.5 cm in total length, 104 cm in effective length) was used with a basic anion buffer. For quantification of ${}^{15}NH_4^+$, the fused silica capillary (75 μ m in inner diameter, 64.5 cm in total length, 56cm in effective length) was used with a cation buffer. The capillaries and buffers used for the analyses were purchased from Agilent. The temperatures of the capillaries used for ${}^{15}NO_2^-/{}^{15}NO_3^-$ and ${}^{15}NH_4^+$ were maintained at 15°C and 25°C, respectively.

Results and discussion

Prepared Sc-TiO₂-AC composites

Figure 1 shows X-ray diffractograms of the Sc-TiO₂-AC composite in comparison with that of Sc-TiO₂. It is clear that the anatase form of TiO₂ crystallite, which has strong

Table 1. Constituents of samples studied and amounts of sample tested for adsorption and photocatalytic activities

Sample	Content (%)	Amount of sample tested (mg)		
	TiO ₂	AC			
AC So TiO	0	100	15.0		
Sc-TiO ₂ -AC	44.2	55.8	10.0 22.6 ^a		

AC, activated carbon; Sc-TiO₂, supercritically treated TiO₂ ^a Amount normalized to contain 10 mg of TiO₂



Fig. 1. X-ray diffractograms of the Sc-TiO₂ (*lower*) and the Sc-TiO₂-AC (*upper*) composites. A, Anatase-type crystallite

photocatalytic activity, was formed in both samples by supercritical treatment.

Table 1 shows the constituents of the samples studied and the amounts of the samples tested. The amount of the Sc-TiO₂-AC was normalized to contain the same amount of TiO₂ (10mg) as the Sc-TiO₂.

Adsorption and photocatalytic activities

Before evaluation of the adsorption and photocatalytic activities of the samples, the adsorption of $^{15}NH_3$ by the evaluation apparatus was studied. Changes in $^{15}NH_3$ and $^{15}N_2$ concentrations are shown in Fig. 2. The concentration of $^{15}NH_3$ was found to decrease gradually to 500 ppm, indicating that the apparatus used in this study adsorbed 2000 ppm of $^{15}NH_3$ in 600 min of treatment time.

Figure 3 shows the changes of ${}^{15}NH_3$ and ${}^{15}N_2$ concentrations for AC, as evaluated before and after UV irradiation. Concentration of ${}^{15}NH_3$ decreased with the treatment time, but it did not become zero, even after 600 min. The concentration of ${}^{15}N_2$ remained constant at negligible levels before and after UV irradiation. Furthermore, no other intermediates and end-products were detected after UV irradiation, indicating that the decrease of ${}^{15}NH_3$ concentration was due to adsorption by the AC and the evaluation apparatus.



Fig. 2. Changes in ¹⁵NH₃ and ¹⁵N₂ concentrations against the treatment time before and after ultraviolet (UV) irradiation (*vertical line*) without the samples. ¹⁵NH₃, ¹⁵N₂ concentrations given as ppm in He and O₂ (4:1) as carrier gases; relative humidity 50% at 25°C; initial concentration of ¹⁵NH₃ 2500 ppm; treatment time 600 min



Fig. 3. Changes in ${}^{15}\text{NH}_3$ and ${}^{15}\text{N}_2$ concentrations against the treatment time before and after UV irradiation (*vertical line*) with activated carbon (AC). ${}^{15}\text{NH}_3$, ${}^{15}\text{N}_2$ concentrations given as ppm in He and O₂ (4:1) as carrier gases; relative humidity 50% at 25°C; initial concentration of ${}^{15}\text{NH}_3$ 2500 ppm; treatment time 600 min; amount of AC tested 15.0 mg

Figure 4 shows the changes of $^{15}\rm NH_3$ and $^{15}\rm N_2$ concentrations for Sc-TiO_2. The concentration of $^{15}\rm NH_3$ decreased and disappeared completely after about 450 min, while $^{15}\rm N_2$ and $^{15}\rm N_2O$ concentrations were found to increase gradually after UV irradiation. These results indicate that the $^{15}\rm NH_3$ adsorbed on the Sc-TiO_2 could be photocatalytically decomposed to $^{15}\rm N_2$ and $^{15}\rm N_2O$ by UV irradiation. The possible end-products $^{15}\rm NO$ and $^{15}\rm NO_2$ were not detected during UV irradiation.

These trends were even more enhanced for the Sc-TiO₂-AC composites, as shown in Fig. 5. The ¹⁵NH₃ concentration decreased to zero after 350min. Compared with Sc-TiO₂,



Fig. 4. Changes in ¹⁵NH₃, ¹⁵N₂, and ¹⁵N₂O concentrations against the treatment time before and after UV irradiation (*vertical line*) with supercritically treated TiO₂ (Sc-TiO₂). ¹⁵NH₃, ¹⁵N₂O concentrations given as ppm in He and O₂ (4:1) as carrier gases; relative humidity 50% at 25°C; initial concentration of ¹⁵NH₃ 2500 ppm; treatment time 600 min; amount of Sc-TiO₂ tested 10.0 mg



Fig. 5. Changes in ¹⁵NH₃, ¹⁵N₂, and ¹⁵N₂O concentrations against the treatment time before and after UV irradiation (*vertical line*) with Sc-TiO₂-AC composites. ¹⁵NH₃, ¹⁵N₂, ¹⁵N₂O concentrations given as ppm in He and O₂ (4:1) as carrier gases; relative humidity 50% at 25°C; initial concentration of ¹⁵NH₃ 2500 ppm; treatment time 600 min; amount of Sc-TiO₂-AC tested 22.6 mg

higher concentration of ${}^{15}N_2$ by the decomposition of ${}^{15}NH_3$ could be attained although ${}^{15}N_2O$ concentration was found to be similar to that for Sc-TiO₂. As for Sc-TiO₂, the possible end-products ${}^{15}NO$ and ${}^{15}NO_2$ were not be detected after treatment with Sc-TiO₂-AC.

Other chemical species that might be obtained by decomposition of ¹⁵NH₃, such as ¹⁵NO₃ and ¹⁵NO₂, should be evaluated. These compounds are thought to be retained in the samples because they are not gaseous compounds under ambient conditions. Therefore, the aqueous solution obtained by extraction of the samples after 600 min of treatment was analyzed by CE as shown in Fig. 6. Evidence for the production of ¹⁵NO₃ and ¹⁵NO₂ was observed after photocatalytic decomposition of ¹⁵NH₃ with Sc-TiO₂ and Sc-TiO₂-AC composites. No such evidence was observed after



Migration time (min)

Fig. 6. Electropherograms from capillary electrophoresis (CE) for anion analysis of aqueous extracts of Sc-TiO₂-AC composite, Sc-TiO₂, and AC after 600-min photocatalytic treatment of ¹⁵NH₃ sample. CE used a fused silica capillary at 15°C with a basic anion buffer



Fig. 7. Electropherograms from CE for cation analysis of aqueous extracts of Sc-TiO₂-AC composite, Sc-TiO₂, and AC after 600-min photocatalytic treatment of ¹⁵NH₃ sample. CE used a fused silica capillary at 25°C with a cation buffer

treatment with AC. Furthermore, NH_4^+ was also found by CE as shown in Fig. 7. With the detection of ${}^{15}NH_4^+$ in all samples, it is apparent that some ${}^{15}NH_3$ still remained in the samples without being decomposed.

From these results, the conversion of ${}^{15}NH_3$ based on nitrogen atom after treatment for 600min was calculated and is shown in Table 2. For AC and Sc-TiO₂, conversion of ${}^{15}NH_3$ during photocatalytic reaction to the decomposition products (${}^{15}N_2$, ${}^{15}N_2O$, ${}^{15}NO_2^-$, ${}^{15}NO_3^-$, ${}^{15}NH_4^+$, ${}^{15}NO_2$, and ${}^{15}NO$) was not quantitative (i.e., <100%), meaning some ${}^{15}NH_3$ still remained. As such, the conversion of ${}^{15}NH_3$ was calculated from the total amount of decomposition products. For treatment with Sc-TiO₂-AC composites, the total conversion was over 100% because of experimental error.

Table 2. Conversion of ¹⁵NH₃ based on nitrogen atom after 600-min treatment

Sample	Conversion (%)										
	¹⁵ NH ₃	$^{15}N_{2}$	$^{15}N_2O$	$^{15}\mathrm{NO}_2^-$	$^{15}\mathrm{NO}_3^-$	$^{15}\mathrm{NH_{4}^{+}}$	¹⁵ NO ₂	¹⁵ NO	Total		
AC Sc-TiO2 Sc-TiO ₂ -AC	99.7^{a} 36.4 ^a 0.0	nd 49.0 83.4	nd 2.2 1.5	nd nd 1.1	nd 7.3 11.9	0.3 5.1 10.3	nd nd nd	nd nd nd	100.0 100.0 108.2		

Initial concentration of ${}^{15}NH_3$ in He and O_2 as carrier gases: 2500 ppm. See Table 1 for quantities of samples tested

nd, Not detected

^aCalculated from sum of decomposition products

$$\begin{array}{c} & & & \\$$

Fig. 8. Proposed decomposition pathway of NH₃ during the photocatalytic process. *g*, Gas; *l*, liquid; *s*, solid

It was found that ${}^{15}NH_3$ cannot be converted to other compounds or intermediates on AC, and little ${}^{15}NH_4^+$ was adsorbed on the AC. As shown in Fig. 3, 20% of ${}^{15}NH_3$ still remained in the gas phase without being adsorbed even after 600min of treatment. From Fig. 2, ${}^{15}NH_3$ was found to be adsorbed by the evaluation apparatus used. Therefore, 99.7% of ${}^{15}NH_3$ is thought to exist as gas or to be adsorbed on the evaluation apparatus.

For Sc-TiO₂, 64% of ¹⁵NH₃ can be converted to several compounds as in Table 2. The remaining 36% of ¹⁵NH₃ is perhaps adsorbed on the evaluation apparatus without being decomposed. On the other hand, with Sc-TiO₂-AC composites, all ¹⁵NH₃ was decomposed photocatalytically with high conversion to ¹⁵N₂. These results clearly show that Sc-TiO₂-AC composites have higher photocatalytic activities than Sc-TiO₂.

Based on these results, a pathway for NH₃ decomposition by the composites is presumed as shown in Fig. 8. By oxidation with hydroxyl radicals (\cdot OH) from H₂O or superoxide anions (O⁻, O₂⁻, O₃⁻) from O₂ on TiO₂ under UV irradiation, NH₃ is decomposed to N₂, N₂O, HNO₂, and HNO₃. In the case of the photocatalytic decomposition of NH₃ over a long treatment time, it was found that NO₂⁻ concentration decreased and NO₃⁻ concentration increased. Therefore, some amounts of H¹⁵NO₂ are thought to be converted to H¹⁵NO₃. The total yield of ¹⁵NO₂⁻ and ¹⁵NO₃⁻ is equivalent to that of the ¹⁵NH₄⁺ remaining on the catalyst surface. This indicates that these species exist as salts, ¹⁵NH₄¹⁵NO₂ and ¹⁵NH₄¹⁵NO₃ deposited on the Sc-TiO₂-AC composites.

Among various decomposed compounds from NH_3 as listed in Table 2, NO_2 and NO were not detected in both Sc-TiO₂ and the Sc-TiO₂-AC composites. This result is desirable because those compounds are well-known air pollutants, referred to as NOx. There is no report that NH_4NO_2 or NH_4NO_3 are harmful or toxic to the environment under ambient conditions. N_2O is harmless to humans and is commonly utilized as an anesthetic. However, it has a much stronger greenhouse gas effect than CO_2 . Although the conversion to N_2O is low, it should be decreased further. It is emphasized that harmless N_2 can be produced mainly by the photocatalytic decomposition of NH_3 .

It is expected that Sc-TiO₂-AC composites will be applied as an environmental cleaning material in places with NH_3 odor, such as toilets and livestock facilities. However, as mentioned above, solid NH_4NO_3 and NH_4NO_2 are produced as decomposition products of NH_3 during photocatalytic reaction. Therefore, some treatment, such as washing with water, to remove these compounds from the composites will be necessary to recover photocatalytic activity. The issue of reactivation of the composites will be addressed in future research.

Conclusions

This study found that $Sc-TiO_2$ -AC composites have very high photocatalytic activity for the decomposition of NH₃. In the decomposition process, NH₃ is successfully converted to harmless and odorless compounds.

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