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Supercritically treated TiO₂-activated carbon composites for cleaning ammonia

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Abstract Supercritically treated $TiO₂$ –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 N_2 , N_2O , NO_2^- , and NO_3^- . The main product was harmless N_2 . 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 · Ammonia · 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. $5-7$ $5-7$ 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 $TiO₂$ as photocatalyst. Wang et al. 9 found that degradation of NH₃ was possible with irondoped TiO₂ as a photocatalyst in acidic solution. Little study on gaseous NH₃ decomposition has been performed. Nazir et al[.10](#page-5-0) studied photocatalytic degradation of gaseous $NH₃$ on TiO₂ that was deposited on carbon particles. Mozzanega et al.^{[11](#page-5-0)} reported NH₃ decomposition over TiO₂ at room temperature, using a flow-type evaluation system for photocatalytic activity of $TiO₂$ that was applied in other studies.^{[12,13](#page-5-0)}

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 $TiO₂$ –activated carbon (Sc-TiO₂-AC) composites were studied for their

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adsorption of and photocatalytic activities on gaseous NH3. A decomposition mechanism of $NH₃$ was also studied by determining the intermediates and end-products of $NH₃$ 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 15ml of isopropanol. The mixture was then treated by ultrasonification for 30min, and decanted to remove the supernatant. Subsequently, the TPT-soaked AC was treated in air for the sol-gel reaction for 5h to obtain $TiO₂–AC$ composites. The $TiO₂–AC$ composites were then treated with supercritical isopropanol at 300°C and 12MPa, which were above the critical temperature (T_c = 235°C) and pressure (P_c = 5.37MPa) of isopropanol, for 5min 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 20mg 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 (50ml/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 16 16 from the following equations:

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

$$
AC\left(\% \right) = 100 - (TiO2 content)
$$
 (2)

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

Based on the content of TiO₂ granules and AC from Eqs. 1 and 2, the Sc-TiO₂-AC composites contained the same weight of $TiO₂$ as that of Sc-TiO₂ 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_B filter, operated at 40keV and 30mA, integrating five times.

Evaluation of adsorption and photocatalytic activities

To evaluate the adsorption and photocatalytic activities of the Sc-TiO₂-AC composites on NH₃, a previously developed evaluation apparatus was used.¹⁶ An oven-dried

sample (containing 10 mg of $TiO₂$) was dispersed in ethanol and then spread over the glass surface of a petri dish (58 cm^2) in area) for 30min 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 1.8l of gas that was composed of He and O_2 gases in a volume ratio of 4:1, was humidified with $H₂O$ at 25 \degree 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 15 NH₃ (Taiyo) was used instead of environmental ${}^{14}NH_3$. The gas was then circulated inside the apparatus at a flow rate of 3.6l/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 ${}^{15}NH_3$, 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 40ml/min.

For detection of ^{15}NO and $^{15}NO_2$, 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 (7ml). Subsequently, the resulting aqueous solution was analyzed by capillary electrophoresis (CE, HP3D CE system; Agilent). For quantification of $^{15}NO_2^-$ and $^{15}NO₃$, the fused silica capillary (50 μ m in inner diameter, 112.5cm in total length, 104cm in effective length) was used with a basic anion buffer. For quantification of ${}^{15}NH_4^+$, the fused silica capillary $(75 \mu m)$ in inner diameter, 64.5cm 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](#page-2-0) 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
	TiO ₂	AС	tested (mg)
AC $Sc-TiO2$	θ 100	100	15.0 10.0
$Sc-TiO,AC$	44.2	55.8	22.6°

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 $TiO₂$ (10 mg) 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 NH₃ 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 600min. The concentration of $\mathrm{^{15}N}$, 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 O_2 $(4:1)$ as carrier gases; relative humidity 50% at 25 $^{\circ}$ C; initial concentration of $^{15}NH_3$ 2500 ppm; treatment time 600 min

Fig. 3. Changes in ${}^{15}NH_3$ and ${}^{15}N_2$ concentrations against the treatment time before and after UV irradiation (*vertical line*) with activated carbon (AC). ¹⁵NH₃, ¹⁵N₂ concentrations given as ppm in He and O₂ (4:1) as carrier gases; relative humidity 50% at 25°C; initial concentration of 15 NH₃ 2500 ppm; treatment time 600 min; amount of AC tested 15.0 mg

[Figure 4 s](#page-3-0)hows the changes of $^{15}NH_3$ and $^{15}N_2$ concentrations for Sc-TiO₂. The concentration of ${}^{15}NH_3$ decreased and disappeared completely after about 450 min, while ${}^{15}N_2$ and ${}^{15}N_2O$ concentrations were found to increase gradually after UV irradiation. These results indicate that the ${}^{15}NH_3$ adsorbed on the $Sc-TiO₂$ could be photocatalytically decomposed to ^{15}N , and $^{15}N_2O$ by UV irradiation. The possible end-products ${}^{15}NO$ and ${}^{15}NO_2$ were not detected during UV irradiation.

These trends were even more enhanced for the $Sc-TiO_2$ -AC composites, as shown in [Fig. 5.](#page-3-0) The ${}^{15}NH_3$ concentration decreased to zero after 350 min. Compared with Sc-TiO₂,

Fig. 4. Changes in ${}^{15}NH_3$, ${}^{15}N_2$, and ${}^{15}N_2$ O concentrations against the treatment time before and after UV irradiation (*vertical line*) with supercritically treated TiO₂ (Sc-TiO₂). 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 15 NH₃ 2500 ppm; treatment time 600 min; amount of Sc-TiO₂ tested 10.0mg

Fig. 5. Changes in ¹⁵NH₃, ¹⁵N₂, and ¹⁵N₂O concentrations against the treatment time before and after UV irradiation (*vertical line*) with Sc- $TiO₂AC$ composites. ¹⁵NH₃, ¹⁵N₂, ¹⁵N₂O concentrations given as ppm in He and $O_2(4:1)$ as carrier gases; relative humidity 50% at 25°C; initial concentration of $^{15}NH_3$ 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 $Sc-TiO_2$. As for $Sc-TiO_2$, the possible end-products ^{15}NO and ^{15}NO , were not be detected after treatment with $Sc-TiO-AC$.

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 600min of treatment was analyzed by CE as shown in Fig. 6. Evidence for the production of ${}^{15}NO_3^-$ and ${}^{15}NO_2^-$ was observed after photocatalytic decomposition of $^{15}NH_3$ 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 $^{15}NH_3$ 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 ${}^{15}NH_3$ sample. CE used a fused silica capillary at 25°C with a cation buffer

treatment with AC. Furthermore, $NH₄⁺$ 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.](#page-4-0) For AC and Sc-TiO₂, conversion of ¹⁵NH₃ 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 $(\%)$										
	$^{15}NH.$	$^{15}N_2$	$^{15}N_2O$	$^{15}NO_2^-$	$^{15}NO_2^-$	$^{15}\mathrm{NH}_4^+$	$^{15}NO2$	^{15}NO	Total		
AC $Sc-TiO2$ $Sc-TiO2-AC$	99.7 ^a 36.4° 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 O₂ as carrier gases: 2500 ppm. Se[e Table 1](#page-2-0) for quantities of samples tested

nd, Not detected

a Calculated from sum of decomposition products

$$
N_{2}(g)
$$
\n
$$
N_{13}(g)
$$
\n
$$
N_{2}(g)
$$

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,](#page-2-0) 20% of $^{15}NH_3$ still remained in the gas phase without being adsorbed even after 600 min of treatment. From [Fig. 2,](#page-2-0) ${}^{15}NH_3$ 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 ${}^{15}NH_3$ can be converted to several compounds as in Table 2. The remaining 36% of $^{15}NH_3$ is perhaps adsorbed on the evaluation apparatus without being decomposed. On the other hand, with $Sc-TiO_2$ -AC composites, all ${}^{15}NH_3$ was decomposed photocatalytically with high conversion to ${}^{15}N_2$. 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^-, O_2^-, O_3^+) from O_2 on Ti O_2 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 $H^{15}NO_2$ are thought to be converted to $H^{15}NO_3$. The total yield of $^{15}NO_2^-$ and $^{15}NO_3^-$ is equivalent to that of the ${}^{15}NH_4^+$ remaining on the catalyst surface. This indicates that these species exist as salts, $^{15}NH_4^{15}NO_2$ and $^{15}NH_4^{15}NO_3$ deposited on the Sc-TiO₂-AC composites.

Among various decomposed compounds from $NH₃$ as listed in Table 2, $NO₂$ and $NO₂$ 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 $NH_aNO₂$ or $NH_aNO₃$ 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 $CO₂$. 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 $NH₃$.

It is expected that Sc-TiO₂-AC composites will be applied as an environmental cleaning material in places with $NH₃$ odor, such as toilets and livestock facilities. However, as mentioned above, solid $NH₄NO₃$ and $NH₄NO₂$ are produced as decomposition products of NH₃ 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-TiO₂-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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