Effects of SO$_2$ on selective catalytic reduction of NO with NH$_3$ over a TiO$_2$ photocatalyst

Yamamoto, Akira; Teramura, Kentaro; Hosokawa, Saburo; Tanaka, Tsunehiro

Science and Technology of Advanced Materials (2015), 16(2)

URL: http://hdl.handle.net/2433/198728

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Type: Journal Article

Textversion: publisher

Kyoto University
Effects of SO$_2$ on selective catalytic reduction of NO with NH$_3$ over a TiO$_2$ photocatalyst

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2015 Sci. Technol. Adv. Mater. 16 024901
(http://iopscience.iop.org/1468-6996/16/2/024901)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 130.54.110.72
This content was downloaded on 10/07/2015 at 05:15

Please note that terms and conditions apply.
Focus Issue Paper

Effects of SO₂ on selective catalytic reduction of NO with NH₃ over a TiO₂ photocatalyst

Akira Yamamoto¹, Kentaro Teramura¹,²,³, Saburo Hosokawa¹,² and Tsunehiro Tanaka¹,²

¹ Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
² Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8520, Japan
³ Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

E-mail: teramura@moleng.kyoto-u.ac.jp

Received 25 November 2014, revised 7 January 2015
Accepted for publication 29 January 2015
Published 10 March 2015

Abstract
The effect of SO₂ gas was investigated on the activity of the photo-assisted selective catalytic reduction of nitrogen monoxide (NO) with ammonia (NH₃) over a TiO₂ photocatalyst in the presence of excess oxygen (photo-SCR). The introduction of SO₂ (300 ppm) greatly decreased the activity of the photo-SCR at 373 K. The increment of the reaction temperature enhanced the resistance to SO₂ gas, and at 553 K the conversion of NO was stable for at least 300 min of the reaction. X-ray diffraction, FTIR spectroscopy, thermogravimetry and differential thermal analysis, x-ray photoelectron spectroscopy (XPS), elemental analysis and N₂ adsorption measurement revealed that the ammonium sulfate species were generated after the reaction. There was a strong negative correlation between the deposition amount of the ammonium sulfate species and the specific surface area. Based on the above relationship, we concluded that the deposition of the ammonium sulfate species decreased the specific surface area by plugging the pore structure of the catalyst, and the decrease of the specific surface area resulted in the deactivation of the catalyst.

Keywords: photocatalyst, NH₃-SCR, SO₂

1. Introduction
The emission of nitrogen oxides (NOₓ) causes air pollution problems such as acid rain and photochemical smog. Selective catalytic reduction (SCR) of NOₓ with ammonia (NH₃) is a commercial de-NOₓ process in the stationary and mobile NOₓ emission sources. The main reaction is as follows:

\[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}. \]

In stationary emission sources, the industrial catalyst for the process is vanadium-oxide-based catalysts such as V₂O₅–WO₃/TiO₂ [1, 2]. The catalysts show high activity and high selectivity to N₂ in the temperature window of 523–673 K. This type of catalyst has to be installed upstream to the particulate collector and to the flue-gas desulfurization...
photocatalyst for the resistance to SO2 gas has not been identified by our group [11, 17], and a kinetic study using an annular fixed bed reactor [15]. Other research groups also carried out a theoretical study [16], which verified the proposed reaction mechanism by our group [11, 17], and a kinetic study using an annular fixed-film photoreactor [18]. However, the potential of the photocatalyst for the resistance to SO2 gas has not been investigated yet, although the resistance is essential to make the photo-SCR system practicable. Thus, our objective is to investigate the effect of SO2 gas on the performance of photo-SCR over the TiO2 photocatalyst. In addition, the systematic characterization of the catalyst after the reaction was carried out to elucidate the deactivation mechanism of the TiO2 photocatalyst.

2. Experimental details

2.1. Materials

The TiO2 (ST-01) powder was purchased from Ishihara Sangyo Kaisha, Ltd. Before use, the TiO2 powder was hydrated in distilled water for 2 h at 353 K and then evaporated to dryness at 353 K. The powder after the hydration was tableted (diameter 20 mm) and calcined at 673 K for 3 h in a furnace under a dry air flow. The tablet was granulated using 25 and 50 mesh sieves to obtain the granules with a diameter of 300–600 μm. Ammonium sulfate (wako) and sodium sulfate (wako) were used as reference samples without further purification.

2.2. Photocatalytic reaction

Photo-SCR was carried out using a conventional fixed bed flow reactor at an atmospheric pressure in the same way as in our previous reports [14]. A quartz reactor was used for the reaction, and the reactor volume was 0.12 mL (12 × 10 × 1 mm). 110 mg of TiO2 granules with a diameter of 300–600 μm were introduced to the reactor and pretreated at 673 K in a 10% O2/He gas at a flow rate of 50 mL min⁻¹ for 60 min. The reaction gas composition was as follows: NO (1000 ppm), NH3 (1000 ppm), O2 (2%), SO2 (300 ppm, if present), He balance. A 200 W Hg–Xe lamp equipped with fiber optics, collective lens and a mirror (San-Ei Electric Co., Ltd, UVF-204 S type B) was used as a light source. The measured light irradiance was 360 mW cm⁻². N2 and N2O products were analyzed by a SHIMADZU GC-8A TCD gas chromatograph with MS-5A and Porapak Q columns, respectively.

2.3. Characterization

The crystalline phase of the TiO2 powder was determined by the x-ray diffraction (XRD) technique using a Rigaku Ultima IV x-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The crystallite size was determined from the full width at half maximum (FWHM) of the diffraction peak of the anatase TiO2 (101) plane (2θ = 25.2°) using the Scherrer equation. The Fourier transform infrared (FTIR) transmission spectra were recorded on a JASCO FT/IR–4200 spectrometer at room temperature at a spectral resolution of 4 cm⁻¹, accumulating 16 scans. The background spectrum was measured without any sample in air and was subtracted from the sample spectra. The catalysts before and after the reaction and the reference samples (ammonium sulfate and sodium sulfate) were diluted with KBr by the sample-to-KBr ratio of 1:5:98.5 and 0.2:99.8 (w/w), respectively, and then pressed into pellets. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed on a Rigaku Thermo plus TG 8120 apparatus at a heating rate of 5 K min⁻¹ under a dry air flow condition at a flow rate of 80 mL min⁻¹ in the range of 298–1173 K using Al2O3 pans. The XPS measurement was conducted on a Shimadzu ESCA-3400 spectrometer. Samples were mounted on a silver sample holder using a conductive carbon tape and were analyzed using Mg Kα radiation in a vacuum chamber in 0.1 eV steps. The position of the carbon peak (284.6 eV) for C1s was used to calibrate the binding energy for all the samples. The surface composition was estimated by the band areas of the XP spectrum of S2p, N1s, Ti2p and O1s and the corresponding relative sensitivity factors [19]. Elemental analyses (EA) were performed on two CHN analyzers (MT-5, Yanaco Co., Ltd and JM10, J-Science Lab Co., Ltd) to analyze the contents of C, H and N, and combustion ion chromatography (Dionex ICS-1500, Mitsubishi Chemical Analytech AQF-2100H) was used to analyze the S content. The N2 adsorption/desorption isotherm was measured using the S内容.
measured at 77 K using liquid nitrogen. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S\textsubscript{BET}). The total specific surface area (S\textsubscript{tot}) and the external specific surface area (S\textsubscript{ext}) were calculated from the linear fitting of the V–t plots (fitting range: 0–0.6 nm for the S\textsubscript{tot} and 3.6–4.6 nm for the S\textsubscript{ext}). The internal specific surface area (S\textsubscript{int}) area for the mesoporous materials was obtained by subtracting the S\textsubscript{ext} from the S\textsubscript{tot}. The pore-sized distribution was calculated from the Barrett–Joyner–Halenda (BJH) plots.

### 3. Results and discussion

#### 3.1. Effect of SO\textsubscript{2} addition on the activity of the photo-SCR

Figure 1 shows the time course of the photo-SCR over the TiO\textsubscript{2} photocatalyst under illumination in the presence or absence of SO\textsubscript{2} (300 ppm) gas at various temperatures. The conversion of NO was stable for 300 min at 433 K in the absence of SO\textsubscript{2} gas, as we reported previously [14]. In the presence of SO\textsubscript{2} at 433 K, the conversion of NO decreased with the reaction time, which indicates that the SO\textsubscript{2} poisoned the catalyst, as in the case of the Mn-based catalysts [9]. The reaction temperature had a significant effect on the deactivation rate of the TiO\textsubscript{2} photocatalyst. At 373 K, the conversion decreased more rapidly than at 433 K, and the conversion was almost stable for at least 300 min at 553 K. For simplification, the sample before the reaction was abbreviated as BR, and the samples after the reactions at 373 K, 433 K and 553 K were abbreviated as AR-373K, AR-433K and AR-553K, respectively.

#### 3.2. XRD patterns

The XRD patterns of the catalysts are shown in figure 2. In all the catalysts, only the diffraction pattern of anatase TiO\textsubscript{2} was observed. Crystalline sizes of anatase TiO\textsubscript{2} were estimated by the Scherrer equation using the diffraction peaks of (101), and the results are listed in table 1. The crystalline size did not change (about 15 nm) after the reaction, revealing that the aggregation of TiO\textsubscript{2} particles did not occur under the reaction conditions at all the reaction temperatures.

#### 3.3. N\textsubscript{2} adsorption/desorption experiments

In N\textsubscript{2} adsorption/desorption experiments at 77 K (figure S1), all the samples exhibited a typical IV-type isotherm and had a vertically long hysteresis loop in the relative pressure (P/P\textsubscript{0}) range of 0.8–1.0, suggesting that all the samples had a porous structure. The pore-sized distribution of the catalyst before the reaction had a sharp peak at 10 nm (figure S2(A)), and the size was the same order of the crystalline size of TiO\textsubscript{2} (15 nm). These results indicate that the mesopores were formed by the gaps between primary TiO\textsubscript{2} particles. The peak became smaller after the reaction in the presence of SO\textsubscript{2} gas. The specific surface area calculated from the V–t plots (figure S3(B)) is summarized in table 1. The S\textsubscript{total} calculated from the V–t plots was in good agreement in the S\textsubscript{BET}. The S\textsubscript{ext} of all the samples was estimated from the V–t plots as 9.0–10.8 m\textsuperscript{2} g\textsuperscript{-1}. The S\textsubscript{int} was calculated by subtracting the S\textsubscript{ext} from the S\textsubscript{tot}. The S\textsubscript{int} was 76.2–112 m\textsuperscript{2} g\textsuperscript{-1}, which shows

---

**Table 1. Crystalline size and specific surface area of catalysts.**

| Sample | d\textsuperscript{a} (nm) | S\textsubscript{BET}\textsuperscript{b} (m\textsuperscript{2} g\textsuperscript{-1}) | S\textsubscript{tot}\textsuperscript{c} (m\textsuperscript{2} g\textsuperscript{-1}) | S\textsubscript{ext}\textsuperscript{d} (m\textsuperscript{2} g\textsuperscript{-1}) | S\textsubscript{int}\textsuperscript{e} (m\textsuperscript{2} g\textsuperscript{-1}) |
|--------|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| BR     | 15.2           | 121                             | 123                             | 10.6                             | 112                             |
| AR-373K | 15.0           | 84.3                            | 87.0                            | 10.8                             | 76.2                             |
| AR-433K | 15.2           | 96.6                            | 99.6                            | 9.0                              | 90.6                             |
| AR-553K | 15.3           | 115                             | 118                             | 9.0                              | 109                             |

\(\textsuperscript{a}\) Crystalline size calculated from the FWHM of the diffraction peak of the anatase TiO\textsubscript{2} (101) plane.

\(\textsuperscript{b}\) Specific surface area determined by N\textsubscript{2} adsorption isotherm at 77 K using the BET method.

\(\textsuperscript{c}\) Total specific surface area calculated from the V–t plots.

\(\textsuperscript{d}\) External specific surface area calculated from the V–t plots.

\(\textsuperscript{e}\) Internal specific surface area calculated by subtracting the external specific surface area from the total specific surface area.
that the largest part of the $S_{\text{tot}}$ was derived from the mesopores.

### 3.4. FTIR spectra

Figure 3(A) shows the FTIR spectra of the catalysts in the region of 900–1800 cm$^{-1}$. In all the catalysts, a band at 1633 cm$^{-1}$ was observed and was attributed to the deformation vibration of water molecules adsorbed on the TiO$_2$ surface. Several bands at 1401, 1242, 1116, 1054 and 978 cm$^{-1}$ appeared after the reaction in the presence of SO$_2$ at 373 K. The sharp band at 1401 cm$^{-1}$ was assigned to the bending vibration of ammonium (NH$_4^+$) ions [20] and was also observed in the case of the reference (NH$_4$)$_2$SO$_4$ powder. Free sulfate ions (SO$_4^{2-}$, $T_d$ symmetry) show two infrared peaks at 1104 ($\nu_3$) and 613 ($\nu_4$) cm$^{-1}$ [20]. The band at 1116 cm$^{-1}$ was due to $\nu_3$ vibration of free sulfate ions and was also observed in both the cases of (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_4$. When a SO$_4^{2-}$ ion is bound to the TiO$_2$ surface, the symmetry can be lowered to either $C_{3v}$ or $C_{2v}$. The lowering symmetry causes the split of the $\nu_3$ vibration band into two peaks for a $C_{3v}$ symmetry and splits into three peaks for a $C_{2v}$ symmetry [20]. Thus, the bands at 1242, 1054 and 978 cm$^{-1}$ are assigned to the surface-coordinated SO$_4^{2-}$ ions. The surface-coordinated SO$_4^{2-}$ ions could have the $C_{2v}$ symmetry based on the number of bands. The SO$_4^{2-}$ ion with a $C_{2v}$ configuration is either chelating bidentate or bridge bidentate [20]. In AR-433K, the shape of the spectrum was similar to that of AR-373K, although the absorbance of the bands at 1401 and 1116 cm$^{-1}$ were slightly weaker than those of AR-373K. In AR-553K, the band at 1116 cm$^{-1}$ disappeared, which means that the deposition of free sulfates was inhibited in the reaction at 553 K, although the other bands at 1401, 1054 and 978 cm$^{-1}$ remained. In the region of 2400–4000 cm$^{-1}$ (figure 3(B)), three adsorption bands at 3425, 3136 and 3023 cm$^{-1}$ were observed after the reaction at 373 K. The broad band between 3600–2800 cm$^{-1}$ is the stretching vibration of OH groups derived from surface hydroxyl groups and adsorbed water molecules, which also appeared in the sample before the reaction. The other two bands were observed in the catalysts after the reaction. The bands at 3136 and 3023 cm$^{-1}$ are attributed to the asymmetric stretching vibration ($\nu_2$) and symmetric stretching vibration ($\nu_1$) of the NH$_4^+$ ions, respectively. The two bands also appeared in the case of (NH$_4$)$_2$SO$_4$, which strongly advocated the generation of NH$_4^+$ ions after the reaction. The peak intensity at 3136 and 3023 cm$^{-1}$ decreased as the reaction temperature increased, which was consistent with the decrease of the band at 1401 cm$^{-1}$ in figure 3(A). The FTIR results clearly revealed the generation of the free and surface-coordinated SO$_4^{2-}$ ions and NH$_4^+$ ions on the TiO$_2$ surface after the reaction. The conversion of NO after 300 min of the reaction decreased in the following order: AR-553K (80.1%) > AR-433K (37.2%) > AR-373K (12.9%). The order was consistent with that of the peak intensities of the free SO$_4^{2-}$ ions and NH$_4^+$ ions, which suggests that the generation of ammonium sulfate species (e.g. (NH$_4$)$_2$SO$_4$ and (NH$_4$)HSO$_4$) induced the deactivation of the catalyst.

### 3.5. TG-DTA analysis

TG profiles of the catalysts are shown in figure 4(A). Several steps of the weight loss were observed in all the catalysts after the reaction, although the TiO$_2$ has only one step of the weight loss around 330 K. From room temperature to 1173 K, the weights of BR, AR-373K, AR-433K and AR-553K decreased by 3.9, 16.1, 12.5 and 8.1%, respectively. Figure 4(B) shows the DTA profiles of the catalysts. All the profiles had a strong exothermic band around 1150 K without the weight loss, which was derived from the phase transition of TiO$_2$ from anatase to rutile. The DTA profile of BR (see the inset of figure 4(B)), a broad exothermic band was observed around 820 K without the weight loss. The peak was observed in all the catalysts before and after the reaction and was possibly due to the crystallization of TiO$_2$ [21].
addition, other exothermic bands were observed around 500 and 700 K in the case of the catalysts after the reaction. Figure 4(C) shows the first derivatives of the TG profiles (DTG) in figure 4(A). The negative band around 330 K was observed in all the catalysts and was assigned to desorption of molecular water. Other weight loss peaks were observed around 496 K, 648 K, 740 and 940 K. DTG profiles of the (NH₄)₂SO₄ powder and a physical mixture sample of the (NH₄)₂SO₄ powder and the TiO₂ powder are also shown in figure 4(C). In the (NH₄)₂SO₄ powder, two peaks were observed at 530 K and 620 K, which were attributed to the following reactions: (1) and (2), respectively [22]

\[
2(NH_4)_2SO_4 \rightarrow (NH_4)_2S_2O_7 + 2NH_3 + H_2O \quad (1)
\]

\[
3(NH_4)_2S_2O_7 \rightarrow 6SO_2 + 2NH_3 + 2N_2 + 9H_2O. \quad (2)
\]

In the physical mixture sample of the (NH₄)₂SO₄ powder and the TiO₂ powder, the weight loss profile had negative peaks around 313 K, 508 K, 648 K, 760 K and 940 K, and the peak positions were in good agreement with those of the profile of AR-373 K. The analogy of the profiles strongly supports the generation of the (NH₄)₂SO₄ species on the TiO₂ surface after the reaction at 373 K. The bands around 500 K and 650 K decreased as the reaction temperature increased from 373 K to 553 K, which suggests that the increase of the reaction temperature inhibits the deposition of the (NH₄)₂SO₄ species on the TiO₂ surface.

3.6. XPS

In the S 2p XP spectra of BR (figure 5(A)), no band was observed in the range of 165–175 eV. In all the catalysts after the reaction, asymmetric bands were observed at the peak position of 168.6–168.8 eV. The asymmetry of the bands is because of the overlap of the split sublevels of the 2pₓ₂ and 2pᵧ₂ states of S atoms (separation of bands: 1.2 eV) by spin–orbit coupling [23]. The spectra of the catalysts after the reaction were reasonably fitted using two Gaussian functions (figure S3 in the supplementary data and table S1). In all the catalysts after the reaction, the peak positions were 168.5–168.6 and 169.7–169.9 eV, which corresponded to the peak positions of S 2p₃/₂ and S 2p₁/₂ of the sulfate (SO₄²⁻) species, respectively [20]. The ratios of the peak areas of S 2p₃/₂ to those of S 2p₁/₂ were 1.96–1.99 in all the catalysts after the reaction, and the values were in good agreement with the theoretical value of 2. The FWHM of the each peak was the same in all the catalysts (about 1.6 eV), which suggests that the S 2p XP spectra of the catalysts are derived from a single sulfur species of SO₄²⁻ (S⁶⁺).

The N 1s XP spectra are shown in figure 5(B). The peak positions of the N bands of the NO₂ and NO₃ species on the TiO₂ surface were reported to be 403.5 eV and 407.0 eV, respectively [24, 25]. There was no band in the region of 403.5–407.0 eV, indicating that the NO₂ and NO₃ species did not exist in all the catalysts after the reaction. In AR-373K, there were two bands with the peak positions at 399.9 and 401.8 eV. The shoulder band at 399.9 eV was attributed to N
atoms of NH$_3$ adsorbed on Lewis acid sites of TiO$_2$, and the band at 401.8 eV was attributed to N atoms of the NH$_4^+$ species adsorbed on Brønsted acid sites and/or ammonium salts [20]. The band at 401.8 eV decreased with increasing the reaction temperature and disappeared in the spectrum of AR-533K.

In the Ti 2p XP spectra (figure 5(C)), the binding energies of the band of Ti 2p$_{1/2}$ and 2p$_{3/2}$ were 458.6–558.8 and 464.4–464.6 eV in all the catalysts before and after the reaction (table S2 in the supplementary data). The values were consistent with those reported in the literature [20]. The O 1s XPS bands (figure 5(D)) of BR were fitted by two Gaussian functions. The peak positions of the two bands were 530.9 eV and 529.8 eV. The band with a higher binding energy of 530.9 eV was due to the O atom of water molecules adsorbed on the surface and surface hydroxyl groups, and the band at 529.8 eV corresponded to the lattice oxygen on the TiO$_2$ surface [26]. The spectra of the samples after the reaction were fitted using two Gaussians. The result of the fitting is shown in table S3. The relative intensities of the higher energy band to the lower energy band increased after the reaction, which was interpreted by the generation of sulfate species because the oxygen atoms in sulfate have a band at 532.4 eV, as shown in figure S4 in the supplementary data.

Table 2 shows the surface composition estimated by the XPS analysis. The ratio of S atoms to Ti atoms (S/Ti) decreased in the order of AR-373K > AR-433K > AR-553K. The N atoms to Ti atoms (N/Ti) ratio also decreased with increasing the reaction temperature. The decreases of the S/Ti and N/Ti ratio should be mainly due to the decomposition of the (NH$_4$)$_2$SO$_4$ species based on the FTIR and TG-DTA analyses. The ratio of N atoms to S atoms (N/S) decreased from 0.41 (373 K) to 0.10 (553 K) with the reaction temperature. The N/S values of the catalysts were lower than that of (NH$_4$)$_2$SO$_4$ powder (0.85). The low N/S values of the catalysts suggests the existence of sulfur species other than (NH$_4$)$_2$SO$_4$. From the XPS analysis, SO$_3^{2-}$ species were not detected, and the valence of all the sulfur species was +6. The FTIR spectroscopy revealed the generation of the surface-coordinated SO$_4^{2-}$ species with the $C_{2v}$ and/or $C_{3v}$ symmetries. Thus, the low N/S values were due to the generation of the surface-coordinated SO$_4^{2-}$ species. Based on the above discussion, the decrease of the N/S values with the increase of the reaction temperature is interpreted by the preferential decrease of the (NH$_4$)$_2$SO$_4$ species compared to the surface-coordinated SO$_4^{2-}$ species with increasing the reaction temperature.
3.7. Elemental analysis (EA)

Concentrations of sulfur atoms and nitrogen atoms were estimated by EA (table 3). The concentration of S atoms and N atoms increased after the reaction and decreased with increasing the reaction temperature. The tendency corresponded to the results of XPS analysis. Surface densities of each atom were calculated by dividing the concentrations by the BET specific surface area of BR (table 1). The surface density of the Ti atoms was calculated to be 7.0 nm$^{-2}$ using a (100) plane of anatase TiO$_2$ [27] and the BET specific surface area of BR. In AR-373K, the surface densities of sulfur atoms and nitrogen atoms were 5.5 and 9.3 nm$^{-2}$, respectively, and the sum of the values were almost twice as much as that of Ti atoms. The result suggests the generation of a bulk (NH$_4$)$_2$SO$_4$ species. The N/S ratio estimated by EA (table 3) had the same tendency as that evaluated by XPS: the N/S ratio decreases with increasing the reaction temperature. In AR-373K, the N/S ratio was 1.7 and was close to 2, which was the theoretical value of the chemical composition of (NH$_4$)$_2$SO$_4$. FTIR, TG-DTA, XPS and EA revealed the generation of the bulk (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface after the reaction. The amount of (NH$_4$)$_2$SO$_4$ in AR-373K, which contains the largest amount of S and N atoms among the three catalysts after the reaction, is calculated to be 12 wt% assuming that all the N atoms, which were estimated by EA, exist in the (NH$_4$)$_2$SO$_4$ form. However, the XRD diffraction peak of the bulk (NH$_4$)$_2$SO$_4$ species was not observed in AR-373K, which implies that the generated bulk (NH$_4$)$_2$SO$_4$ species has an amorphous structure. Thus, the generated bulk (NH$_4$)$_2$SO$_4$ species plugged the pores of the catalysts, which resulted in the decrease of the $S_{\text{tot}}$ (figure 6).

The amount of the (NH$_4$)$_2$SO$_4$ species decreased with increasing the reaction temperature. Figures 7(A) and (B) show a correlation between the $S_{\text{tot}}$ and the contents of N and S estimated by the EA. The increment of the contents of S and N drastically decreased the $S_{\text{tot}}$. FTIR analysis revealed two $\text{SO}_4^{2-}$ species: one is the (NH$_4$)$_2$SO$_4$ species and the other is the surface-coordinated $\text{SO}_4^{2-}$ species. The negative linear correlation for the N content strongly suggests that the decrease of the $S_{\text{tot}}$ is not because of the generation of the surface-coordinated $\text{SO}_4^{2-}$ species but is because of the bulk (NH$_4$)$_2$SO$_4$ species. The conversion of NO after 300 min of the reaction was plotted vs. the $S_{\text{tot}}$ (figure 8). The strong

### Table 3. Results of elemental analysis.

| Sample     | S (at%) | N (at%) | S (nm$^{-2}$) | N (nm$^{-2}$) | N/S (atom/atom) |
|------------|---------|---------|---------------|---------------|-----------------|
| BR         | 0.06    | 0       | 0.09          | 0             | 0               |
| AR-373K    | 3.5     | 2.6     | 5.5           | 9.3           | 1.7             |
| AR-433K    | 2.6     | 1.6     | 4.1           | 5.6           | 1.4             |
| AR-553K    | 1.7     | 0.64    | 2.7           | 2.3           | 0.85            |

3.8. Structure of the ammonium sulfate species and deactivation mechanism

N$_2$ adsorption/desorption experiments revealed the decrease of the $S_{\text{tot}}$ after the reaction, which was mainly due to the decrease of the $S_{\text{int}}$. The decrease of the $S_{\text{int}}$ is not due to the aggregation of the TiO$_2$ particles during the reaction because the crystalline size of the TiO$_2$ particles did not change after the reaction (table 1). FTIR, TG-DTA, XPS and EA revealed the generation of the bulk (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface after the reaction. The amount of (NH$_4$)$_2$SO$_4$ in AR-373K, which contains the largest amount of S and N atoms among the three catalysts after the reaction, is calculated to be 12 wt% assuming that all the N atoms, which were estimated by EA, exist in the (NH$_4$)$_2$SO$_4$ form. However, the XRD diffraction peak of the bulk (NH$_4$)$_2$SO$_4$ species was not observed in AR-373K, which implies that the generated bulk (NH$_4$)$_2$SO$_4$ species has an amorphous structure. Thus, the generated bulk (NH$_4$)$_2$SO$_4$ species plugged the pores of the catalysts, which resulted in the decrease of the $S_{\text{tot}}$ (figure 6).

The amount of the (NH$_4$)$_2$SO$_4$ species decreased with increasing the reaction temperature. Figures 7(A) and (B) show a correlation between the $S_{\text{tot}}$ and the contents of N and S estimated by the EA. The increment of the contents of S and N drastically decreased the $S_{\text{tot}}$. FTIR analysis revealed two $\text{SO}_4^{2-}$ species: one is the (NH$_4$)$_2$SO$_4$ species and the other is the surface-coordinated $\text{SO}_4^{2-}$ species. The negative linear correlation for the N content strongly suggests that the decrease of the $S_{\text{tot}}$ is not because of the generation of the surface-coordinated $\text{SO}_4^{2-}$ species but is because of the bulk (NH$_4$)$_2$SO$_4$ species. The conversion of NO after 300 min of the reaction was plotted vs. the $S_{\text{tot}}$ (figure 8). The strong

![Figure 6. Deposition model of sulfate species of the catalysts.](image-url)
positive and linear correlation was obtained, which indicates that the decrease of the $S_{\text{tot}}$ results in the decrease of the conversion of NO. Based on the above discussion, we concluded that the generation of the (NH$_4$)$_2$SO$_4$ species plugged a part of the mesopores derived from the gap between the TiO$_2$ particles, which resulted in the decrease of the $S_{\text{tot}}$ and the deactivation of the catalyst.

4. Conclusions

In this study, tolerance to SO$_2$ gas was investigated in the photo-SCR of NO with NH$_3$ over the TiO$_2$ photocatalyst. The introduction of SO$_2$ drastically decreased the conversion of NO at 373 K. The increment of the reaction temperature drastically improved the stability of the catalyst, and at 553 K, the deactivation was not observed for 300 min of the reaction. FTIR and XPS results suggest that two SO$_4^{2-}$ species exist on the TiO$_2$ surface: the surface-coordinated SO$_4^{2-}$ species and the free SO$_4^{2-}$ species as a bulk (NH$_4$)$_2$SO$_4$ formed after the photocatalytic reaction. The deactivation occurs due to a pore plugging by the deposition of the (NH$_4$)$_2$SO$_4$ species on the TiO$_2$ surface on the basis of the correlation among the contents of N and S atoms after reaction, the $S_{\text{tot}}$ estimated by V–t plots and the photocatalytic activity.

Acknowledgments

This study was partially supported by the Program for Element Strategy Initiative for Catalysts & Batteries (ESICB), commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and the Pre-curser Research for Embryonic Science and Technology (PRESTO), supported by the Japan Science and Technology Agency (JST). Akira Yamamoto thanks the JSPS Research Fellowships for Young Scientists.

References

[1] Bosch H and Janssen F 1988 Formation and control of nitrogen oxides Catal. Today 2 369
[2] Busca G, Lietti L, Ramis G and Berti F 1998 Chemical and mechanistic aspects of the selective catalytic reduction of NO$_x$ by ammonia over oxide catalysts: a review Appl. Catal. B 18 1
[3] Singoredjo L, Korver R, Kapteijn F and Moulijn J 1992 Alumina supported manganese oxides for the low-temperature selective catalytic reduction of nitric oxide with ammonia Appl. Catal. B 1 297
[4] Kapteijn F, Singoredjo L, Andreini A and Moulijn J A 1994 Activity and selectivity of pure manganese oxides in the selective catalytic reduction of nitric oxide with ammonia Appl. Catal. B 3 173
[5] Long R Q, Yang R T and Chang R 2002 Low temperature selective catalytic reduction (SCR) of NO with NH$_3$ over Fe-Mn based catalysts Chem. Commun. 452
[6] Li J, Chen J, Ke R, Luo C and Hao J 2007 Effects of precursors on the surface Mn species and the activities for NO reduction over MnO$_x$/TiO$_2$ catalysts Catal. Commun. 8 1896
[7] Tang X, Hao J, Yi H and Li J 2007 Low-temperature SCR of NO with NH₃ over AC/C supported manganese-based monolithic catalysts Catal. Today 126 406

[8] Li J, Chang H, Ma L, Hao J and Yang R T 2011 Low-temperature selective catalytic reduction of NOₓ with NH₃ over metal oxide and zeolite catalysts— a review Catal. Today 175 147

[9] Sjoerd Kijlstra W, Biervliet M, Poels E K and Bliek A 1998 Deactivation by SO₂ of MnOₓ/Al₂O₃ catalysts used for the selective catalytic reduction of NO with NH₃ at low temperatures Appl. Catal. B 16 327

[10] Yamazoe S, Okumura T, Teramura K and Tanaka T 2006 Development of the efficient TiO₂ photocatalyst in photoassisted selective catalytic reduction of NO with NH₃ Catal. Today 111 266

[11] Teramura K, Tanaka T and Funabiki T 2003 Photoassisted selective catalytic reduction of NO with ammonia in the presence of oxygen over TiO₂ Langmuir 19 1209

[12] Teramura K, Tanaka T, Yamazoe S, Arakaki K and Funabiki T 2004 Kinetic study of photo-SCR with NH₃ over TiO₂ Appl. Catal. B 53 29

[13] Yamazoe S, Masutani Y, Teramura K, Hitomi Y, Shishido T and Tanaka T 2008 Promotion effect of tungsten oxide on photo-assisted selective catalytic reduction of NO with NH₃ over TiO₂ Appl. Catal. B 83 123

[14] Yamamoto A, Mizuno Y, Teramura K, Shishido T and Tanaka T 2013 Effects of reaction temperature on the photocatalytic activity of photo-SCR of NO with NH₃ over a TiO₂ photocatalyst Catal. Sci. Technol. 3 1771

[15] Yamamoto A, Mizuno Y, Teramura K, Hosokawa S, Shishido T and Tanaka T 2015 Visible-light-activated selective catalytic reduction of NO with NH₃ on porphyrin derivative-modified TiO₂ photocatalysts Catal. Sci. Technol. 5 556

[16] Ji Y and Luo Y 2014 First-principles study on the mechanism of photoselective catalytic reduction of NO by NH₃ on anatase TiO₂(101) surface J. Phys. Chem. C 118 6359

[17] Yamazoe S, Teramura K, Hitomi Y, Shishido T and Tanaka T 2007 Visible light absorbed NH₂ species derived from NH₃ adsorbed on TiO₂ for photoassisted selective catalytic reduction J. Phys. Chem. C 111 14189

[18] Chou Y and Ku Y 2012 Selective reduction of NO by photo-SCR with ammonia in an annular fixed-film photoreactor Front. Environ. Sci. Eng. 6 149

[19] Scofield J H 1976 Hartree–Slater subshell photoionization cross-sections at 1254 and 1487 eV J. Electron Spectrosc. Relat. Phenom. 8 129

[20] Chen J P and Yang R T 1993 Selective catalytic reduction of NO with NH₃ on SO₂/TiO₂ superacid catalyst J. Catal. 139 277

[21] Hague D C and Mayo M J 1994 Controlling crystallinity during processing of nanocrystalline titania J. Am. Ceram. Soc. 77 1957

[22] Halstead W D 1970 Thermal decomposition of ammonium sulphate J. Appl. Chem. 20 129

[23] Lindberg B J 1970 Substituent effects of sulfur groups: III. The influence of conjugation on ESCA spectra of sulfur substituted nitrobenzenes Acta Chem. Scand. 24 3661

[24] Rodriguez J A, Jirsak T, Liu G, Hrbek J, Dvorak J and Maiti A 2001 Chemistry of NO₂ on oxide surfaces: formation of NO₃ on TiO₂(110) and NO₂ ↔ O vacancy interactions J. Am. Chem. Soc. 123 9597

[25] Haubrich J, Quiller R G, Benz L, Liu Z and Friend C M 2010 In situ ambient pressure studies of the chemistry of NO₂ and water on rutile TiO₂(110) Langmuir 26 2445

[26] Wagner C D, Ringgs W M, Davis L E and Moulder J F 1979 Handbook of X-Ray Photoelectron Spectroscopy (Eden Prairie, MN: Perkin-Elmer Corp)

[27] Lu Y, Choi D-J, Nelson J, Yang O B and Parkinson B A 2006 Adsorption, desorption, and sensitization of low-index anatase and rutile surfaces by the ruthenium complex dye N₃ J. Electrochem. Soc. 153 E131