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# Deactivation of a Ce/TiO<sub>2</sub> Catalyst by SO<sub>2</sub> in the Selective Catalytic Reduction of NO by NH<sub>3</sub>

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The effects of SO<sub>2</sub> on the selective catalytic reduction of NO by NH<sub>3</sub> over a Ce/TiO<sub>2</sub> catalyst were studied. Conversion of NO remained above 90% in the presence of 100 ppm SO<sub>2</sub> at 350 °C for 48 h. However, when 180 ppm SO<sub>2</sub> was added at 300 °C, NO conversion only remained above 90% during the first 12 h and then gradually decreased with time. Characterizations of fresh and SO<sub>2</sub>-poisoned Ce/TiO<sub>2</sub> catalysts were carried out using Brunauer–Emmett–Teller method, ion chromatography, X-ray photoelectron spectroscopy, and X-ray diffraction. The analytical results indicate that there was no obvious change in the crystal structure of the different samples; however, the specific area decreased with SO<sub>2</sub> poisoning time. Sulfates were formed and preferentially diffused from the surface to a bulk phase during the poisoning process. Temperature-programmed desorption and diffuse reflectance infrared Fourier-transform spectroscopy results show that in the presence of O<sub>2</sub>, SO<sub>2</sub> could react with NH<sub>3</sub> to form NH<sub>4</sub>HSO<sub>4</sub>, which is deposited on the surface of the catalyst and blocked the active sites. Moreover, the main reason for the deactivation is that SO<sub>2</sub> could react with the catalyst to form high thermally stable Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, resulting in the disruption of the redox properties between Ce(IV) and Ce(III) and the inhibition of the formation and adsorption of nitrate species.

## Introduction

Nitrogen oxides (NO<sub>x</sub>) emissions from both stationary and mobile fuel combustion sources pose serious environmental problems because of their contribution to acid rain, photochemical smog, ozone depletion, and greenhouse effects.<sup>1</sup> The selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> is a well-known technique used for the removal of NO<sub>x</sub> from stationary power stations and diesel engines.<sup>2–4</sup> The V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>–MoO<sub>3</sub>/TiO<sub>2</sub><sup>5</sup> catalysts have been widely applied in NO<sub>x</sub> removal according to the following reaction: 4NO + 4NH<sub>3</sub> + O<sub>2</sub> → 4N<sub>2</sub> + 6H<sub>2</sub>O. However, the toxicity of vanadium limits the development of these catalysts. Therefore, many researchers have recently focused on new catalysts, including zeolite and transition metal oxides. Among these, the zeolite catalysts, such as Fe-ZSM-5<sup>6</sup> and Fe-Ce-ZSM-5,<sup>7</sup> have been found to be highly active and selective for the reduction of NO by NH<sub>3</sub> over a broader temperature range and to be stable in the presence of SO<sub>2</sub> and H<sub>2</sub>O. A large number of other transition metal oxide-based systems, such as MnO<sub>x</sub>,<sup>8</sup> Cu/TiO<sub>2</sub>,<sup>9</sup> and Fe<sub>x</sub>TiO<sub>y</sub>,<sup>10</sup> have also been extensively studied and thought to be promising alternatives to the V-based catalysts. We also recently reported a novel Ce/TiO<sub>2</sub> catalyst,<sup>11</sup> which was highly active in the SCR reaction within the temperature range of 275–400 °C and showed an excellent selectivity for N<sub>2</sub>. Since typical coal and diesel fired exhausts contain variable amounts of SO<sub>2</sub>, understanding the effects of SO<sub>2</sub> on SCR activity is important for the development and application of appropriate catalysts. The tolerance of metal oxide based catalysts to SO<sub>2</sub> depends on the type and oxidation state of the deposited metal, the nature of the support, and the kind of reducing agent. For example, chemical transformation of MnO to MnSO<sub>4</sub> was the main reason for the deactivation of the SCR over MnO<sub>x</sub>.<sup>12</sup> In the case of

V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>13</sup> the formation of aluminum sulfate during the SCR reaction in the presence of SO<sub>2</sub> reduced the surface area of the catalyst, which resulted in severe deactivation of the SCR catalyst. Ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>), which is a solid salt, also accumulated on the surface of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and interfered with the SCR reaction.<sup>14</sup> It has been determined that TiO<sub>2</sub> has an excellent sulfur tolerance because it is only partially and reversibly sulfated on its surface during the SCR reaction in the presence of SO<sub>2</sub>.<sup>15</sup> Therefore, for the Ce/TiO<sub>2</sub> catalyst, we focused on the changes in the structure and state of the deposited metal oxides and the interaction between SO<sub>2</sub> and the reactants when the catalyst was exposed to SO<sub>2</sub> in a typical SCR reaction.

In the present study, we investigated the effects of SO<sub>2</sub> on the SCR of NO by NH<sub>3</sub> over the Ce/TiO<sub>2</sub> catalyst, characterizing the poisoned catalysts and the SO<sub>2</sub> poisoning mechanism. Brunauer–Emmett–Teller (BET), ion chromatography (IC), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD) methods were used to characterize the poisoned catalysts and to identify the surface and bulk sulfate species. A SO<sub>2</sub> deactivation process of Ce/TiO<sub>2</sub> in the SCR of NO by NH<sub>3</sub> is proposed using in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).

## Experimental Section

**Catalyst Preparation.** The Ce/TiO<sub>2</sub> catalyst (Ce loading was 20.0 wt %) was prepared by an impregnation method using an anatase type TiO<sub>2</sub> (Shanghai Huijing Co. China) and an aqueous solution of cerium nitrate. The sample was dried at 110 °C for 12 h followed by calcination at 500 °C in air for 3 h. Finally, the catalyst was crushed and sieved to 20–40 mesh size.

**Techniques of Characterization.** The nitrogen adsorption–desorption isotherms were obtained at –196 °C over the whole range of relative pressures, using Quantasorb-18 automatic

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equipment (Quanta Chrome Instrument Co. USA). Specific areas were computed from these isotherms by applying the BET method.

The sulfate formed over the Ce/TiO<sub>2</sub> catalyst was converted into a water-soluble sulfate, and the quantitative analysis was performed using a Metrohm 861 Advanced Compact Ion Chromatograph (IC, Metrohm, Ltd., Switzerland). The corresponding sulfur contents from different samples were calculated from the concentration of SO<sub>4</sub><sup>2-</sup> based on the stoichiometry.

A computerized Rigaku D/max-RB Diffractometer (Japan, Cu K $\alpha$  radiation, 0.154056 nm) was used to obtain XRD patterns. Scans were taken over a range of 2 $\theta$  angles from 10 to 90° at a speed of 4° min<sup>-1</sup>.

The XPS measurement was carried out on an ESCALAB Mark II spectrometer (Vacuum Generators, UK) using Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The binding energy was corrected using the contaminated carbon (284.6 eV).

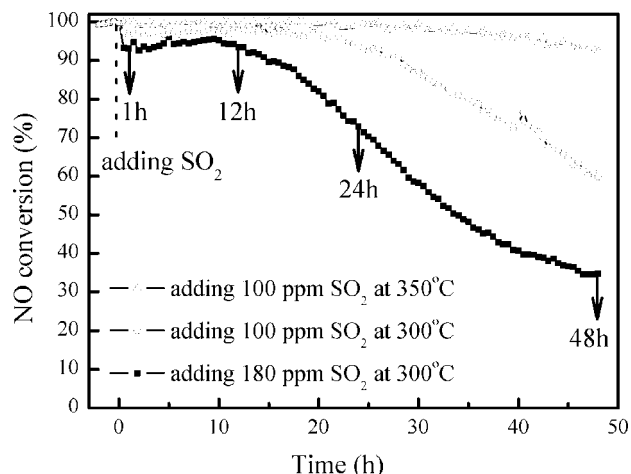
The SO<sub>2</sub> + O<sub>2</sub> TPD experiments were carried out in a flow of He (30 cm<sup>3</sup> min<sup>-1</sup>) over 350 mg of the catalyst. Prior to the TPD experiment, all catalysts were pretreated at 500 °C for 1 h in a flow of 20% O<sub>2</sub>/He to yield a clean surface, followed by cooling to 300 °C. The samples were treated with 4000 ppm SO<sub>2</sub> + 5% O<sub>2</sub>/He (30 cm<sup>3</sup> min<sup>-1</sup>) at 300 °C for 1 h and then purged by He for 30 min to flush the excess SO<sub>2</sub>. During each TPD experiment the sample was heated at a rate of 30 °C min<sup>-1</sup> to the final temperature of 900 °C, and  $m/z$  values of 64 and 32 were monitored online by a mass spectrometer (Hiden HPR20, UK).

In situ DRIFTS was performed with a Nexus 670 (Thermo Nicolet, USA) Fourier-transform infrared (FT-IR) spectrometer equipped with an in situ diffuse reflection chamber and a high-sensitivity mercury–cadmium–telluride (MCT) detector. The sample was finely ground and placed in a ceramic crucible in the in situ chamber. Mass flow controllers and a sample temperature controller were used to simulate the reaction conditions, such as the mixture of gases, pressure, and sample temperature, which were the same as those in the catalytic activity tests. Prior to each experiment, the catalyst was heated in situ in a flow of 5% O<sub>2</sub>/N<sub>2</sub> at 500 °C for 30 min and then cooled to 300 °C. A reference spectrum of the catalyst in a flow of 5% O<sub>2</sub>/N<sub>2</sub> was taken as the background. All the spectra were collected at a resolution of 4 cm<sup>-1</sup> with an accumulation of 100 scans.

**Activity Test.** The catalytic reaction was carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reactor was a 6-mm inside diameter quartz tube with a thermocouple placed on the outside wall of the reactor to control the temperature of the furnace. About 0.6 mL of catalyst (20–40 mesh) was used in all experiments. The reactor was heated by a temperature-controlled furnace. The feed gases consisting of 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol % O<sub>2</sub>, and 100 or 180 ppm SO<sub>2</sub> in N<sub>2</sub> were adjusted by mass flow controllers and introduced into the reactor with a total flow rate of 500 cm<sup>3</sup> min<sup>-1</sup>, yielding a gas hourly space velocity (GHSV) of 50000 h<sup>-1</sup>. Analysis of the NO concentration was carried out using the online Nexus 670 FT-IR spectrometer equipped with a gas cell having a volume of 2 dm<sup>3</sup>.

## Results and Discussion

**Effect of SO<sub>2</sub> on the Catalytic Activity of Ce/TiO<sub>2</sub>.** The effect of the addition of SO<sub>2</sub> on the SCR of NO by NH<sub>3</sub> over the Ce/TiO<sub>2</sub> catalyst was monitored as a function of time on stream at 300 or 350 °C. As shown in Figure 1, a steady-state NO conversion of 99.8% at 350 °C was obtained in the absence



**Figure 1.** Effect of SO<sub>2</sub> on the SCR of NO with NH<sub>3</sub> over 20%Ce/TiO<sub>2</sub> catalyst.

**TABLE 1: Specific Surface Areas and Sulfur Contents of Fresh and Poisoned Ce/TiO<sub>2</sub> Catalysts**

sample (Ce/TiO <sub>2</sub> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	sulfur content (wt %)
S-0 h	128.6	-
S-1 h	124.5	3.00
S-12 h	97.7	6.12
S-24 h	90.8	8.05
S-48 h	82.5	11.76

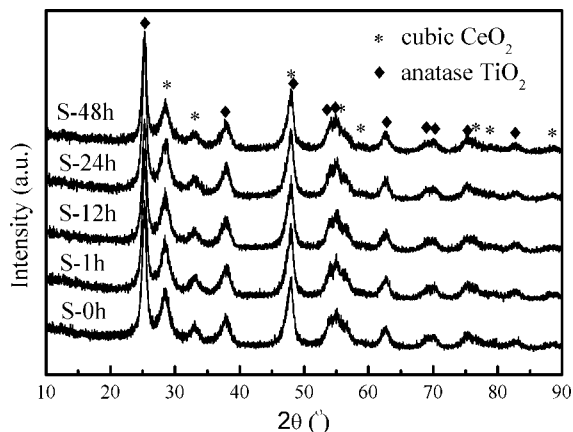
of SO<sub>2</sub>. The addition of 100 ppm SO<sub>2</sub> to the feed resulted in a slight decrease in NO conversion to a certain value of 92.5% after 48 h. In contrast, a more obvious decrease in SCR activity occurred upon the addition of 100 ppm SO<sub>2</sub> at 300 °C. The NO conversion activity declined to 59.8% at 48 h, suggesting that the reaction temperature plays an important role in NO reduction in the presence of SO<sub>2</sub>. Furthermore, NO conversion decreased to 34.5% in the following 48 h when 180 ppm SO<sub>2</sub> was fed at 300 °C. These results demonstrate that the presence of SO<sub>2</sub> considerably deactivates the SCR reaction over Ce/TiO<sub>2</sub>.

To clarify the nature of the effects of SO<sub>2</sub> on the catalyst under different conditions, characterizations of the catalysts were performed. The poisoned catalysts under the reaction condition of 180 ppm SO<sub>2</sub> at 300 °C were chosen because the deactivation of Ce/TiO<sub>2</sub> by SO<sub>2</sub> was remarkable. Fresh and poisoned catalysts with different poisoning times are denoted as S-0 h, S-1 h, S-12 h, S-24 h, and S-48 h, respectively.

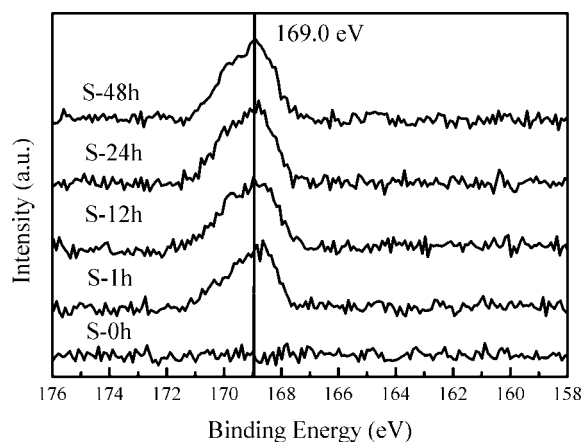
Reaction conditions were as follows: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 5%, SO<sub>2</sub> 100 or 180 ppm, balance N<sub>2</sub>, GHSV = 50000 h<sup>-1</sup>, total flow rate 500 cm<sup>3</sup> min<sup>-1</sup>, temperature 300 or 350 °C

**Characterization of Poisoned Catalysts.** The specific surface areas and sulfur contents of the fresh and poisoned Ce/TiO<sub>2</sub> catalysts are summarized in Table 1. Significant decreases in surface area were observed with increased time after the fresh Ce/TiO<sub>2</sub> catalysts were poisoned by SO<sub>2</sub>. In addition, the sulfur contents of poisoned catalysts determined by IC also increased with poisoning time. It has been demonstrated that when sulfate species are formed and deposited on the catalyst the specific surface area of the catalyst decreases. Our results are consistent with studies<sup>13</sup> that showed that the decreasing surface area of a catalyst is one reason for the decrease in catalytic activity in the presence of SO<sub>2</sub>.

The X-ray powder diffraction patterns of the fresh and poisoned Ce/TiO<sub>2</sub> catalysts are shown in Figure 2. All reflections showed typical diffraction patterns for the TiO<sub>2</sub> anatase phase



**Figure 2.** XRD patterns of fresh and poisoned Ce/TiO<sub>2</sub> catalysts.

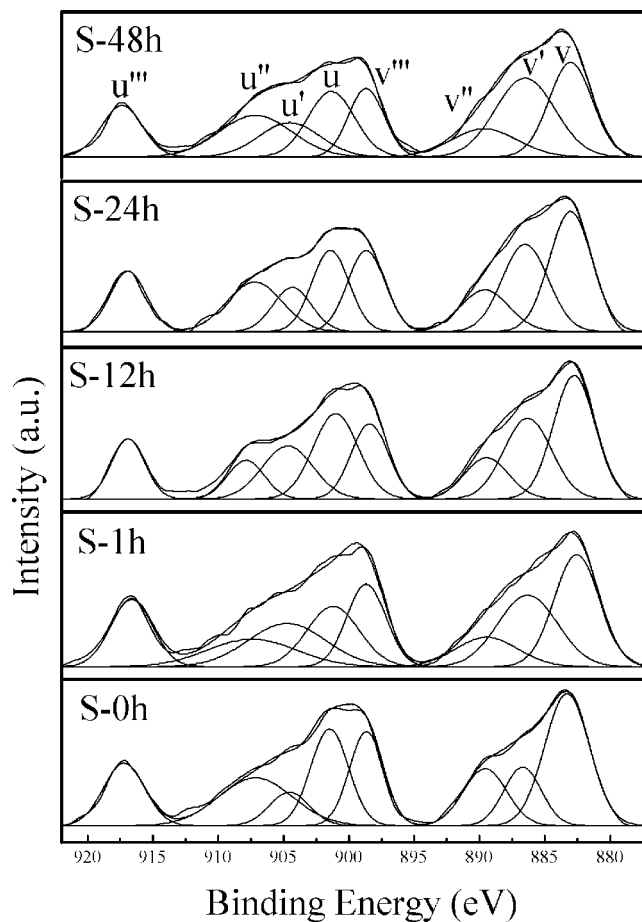


**Figure 3.** Experimental S2p XPS spectra of fresh and poisoned Ce/TiO<sub>2</sub> catalysts.

(PDF-ICDD 21-1272) and the cubic CeO<sub>2</sub> structure (PDF-ICDD 34-0394). With an increase in poisoning time, no obvious change was observed in the crystal structures of the different samples. Although more than 11% sulfur content was detected on the Ce/TiO<sub>2</sub> catalyst poisoned by 180 ppm SO<sub>2</sub> at 300 °C for 48 h, no new peaks ascribed to sulfate were observed, which suggests that either surface sulfate or an amorphous bulk sulfate formed on the surface of the catalyst.<sup>12</sup>

The catalysts were further analyzed using XPS to identify the surface nature and concentration of the active species. The representative photoelectron peaks of S2p and Ce3d pertaining to fresh and poisoned samples are depicted in Figures 3 and 4. The corresponding binding energies of Ce3d<sub>5/2</sub> and S2p<sub>3/2</sub>, together with the Ce(III)/Ce ratio and sulfur weight percentages on the surface determined by XPS, are summarized in Table 2.

An essential difference in the sulfation of Ce/TiO<sub>2</sub> was exhibited in the behavior of the S2p and Ce3d lines. That is, the exposure of the fresh catalyst to SO<sub>2</sub> resulted in an appearance of an S2p feature (Figure 3). The S2p<sub>3/2</sub> binding energies, which are usually applied to elucidate the chemical state of sulfur,<sup>16</sup> are shown in Table 2. These data demonstrate that the S2p<sub>3/2</sub> features were consistent with the S(VI) oxidation state and assigned to the sulfate species.<sup>17–19</sup> In addition, the surface sulfur weight percentages presented in Table 2 were much lower than the total sulfur contents from the corresponding samples (Table 1), suggesting that sulfur preferentially diffuses from the surface to a bulk phase during the poisoning process. In view of the formation of Ce sulfates, the distribution of sulfur is related to the distribution of Ce. Furthermore, the atomic ratio of Ce/Ti (0.074) on the surface of Ce/TiO<sub>2</sub> is lower than the



**Figure 4.** Experimental and fitted Ce3d XPS spectra of fresh and poisoned Ce/TiO<sub>2</sub> catalysts.

**TABLE 2: Binding Energies of Core Electrons and Surface Weight Concentrations on the Samples**

sample (Ce/TiO <sub>2</sub> )	binding energy (eV)		Ce(III)/Ce (%) <sup>a</sup>	S (%) <sup>b</sup>
	Ce3d <sub>5/2</sub> (v')	S2p <sub>3/2</sub>		
S-0 h	886.7		22.8	
S-1 h	886.4	168.7	29.5	1.77
S-12 h	886.3	169.0	28.2	2.41
S-24 h	886.6	168.8	29.1	2.18
S-48 h	886.6	168.9	35.8	2.21

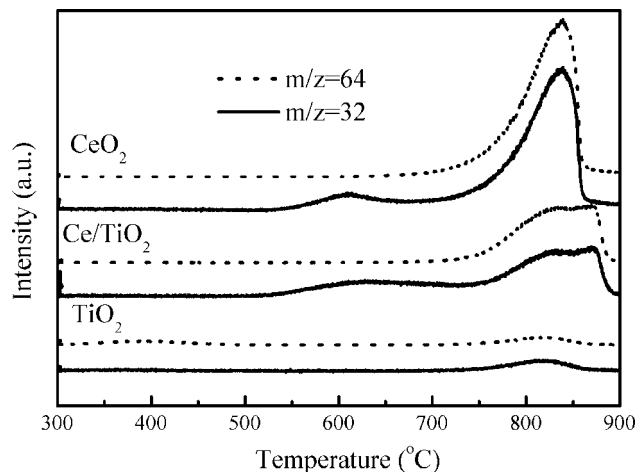
<sup>a</sup> Ce(III)/Ce ratio corresponds to the ratio of the peak area of the v' component relative to the total of the peak areas of all v components. <sup>b</sup> Weight ratio of sulfur on the surface of samples.

calculated value (0.11). Therefore, sulfur preferentially diffused from the surface to a bulk phase because of the limited exposed Ce sites.

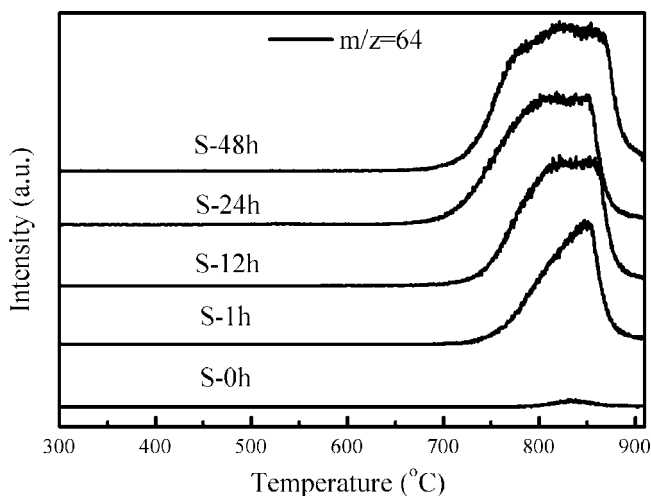
By use of a previously described fitting procedure,<sup>20</sup> complex spectra in the Ce3d region were resolved into eight components. As shown in Figure 4, the peaks labeled *u* are due to 3d<sub>3/2</sub> spin-orbit states, and those labeled *v* are the corresponding 3d<sub>5/2</sub> states. The *u*'/*v*' doublet is attributed to the primary photoemission from Ce(III). The Ce(III)/Ce ratios in Table 2 indicate that a portion of the Ce(IV) ions transformed into Ce(III) ions as a result of Ce/TiO<sub>2</sub> exposure to SO<sub>2</sub>, according to the following reaction:<sup>20</sup> 2CeO<sub>2</sub> + 3SO<sub>2</sub> + O<sub>2</sub> → Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

The O1s and Ti2p XPS spectra were also recorded (data not shown here). The O1s spectra exhibit that both chemisorbed oxygen and lattice oxygen species existed on the catalyst surface.<sup>21</sup> The Ti2p spectra show that titanium was mostly confined to its highest oxidation state (IV).<sup>22,23</sup> No obvious





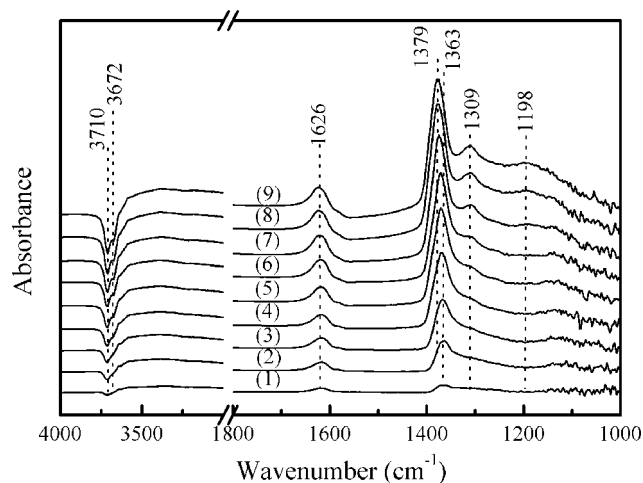
**Figure 5.** SO<sub>2</sub> + O<sub>2</sub> TPD spectra obtained at 64 and 32 amu after Ce/TiO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub> samples were exposed to 4000 ppm SO<sub>2</sub> + 5% O<sub>2</sub> in He for 1 h at 300 °C.



**Figure 6.** SO<sub>2</sub> TPD profiles of fresh and poisoned Ce/TiO<sub>2</sub> catalysts.

difference was observed from the O1s and Ti2p XPS spectra for fresh and poisoned samples.

**TPD Analysis.** To better understand the nature of the sulfate species formed on the poisoned samples, we examined TPD curves for Ce/TiO<sub>2</sub> after exposure to 4000 ppm SO<sub>2</sub> + 5% O<sub>2</sub> in He for 1 h at 300 °C. The SO<sub>2</sub> ( $m/z = 64$ ) and the O<sub>2</sub> ( $m/z = 32$ ) signals were monitored. For comparison, the TPD patterns of TiO<sub>2</sub> and CeO<sub>2</sub> exposed to the same conditions were also recorded. Figure 5 clearly shows two small peaks that appeared at 380 and 813 °C for TiO<sub>2</sub>. Since no O<sub>2</sub> desorption occurred simultaneously with SO<sub>2</sub> desorption below 450 °C, the low temperature peak was assigned to the desorption of molecular SO<sub>2</sub>.<sup>24</sup> The high temperature peak originated from the impurity as demonstrated by the Ce/TiO<sub>2</sub> TPD result (Figure 6) without any pretreatment. In contrast, a large amount of SO<sub>2</sub> desorbed from the surface of CeO<sub>2</sub> in the temperature range of 700–875 °C. These results indicate SO<sub>2</sub> accumulates more on CeO<sub>2</sub> than on TiO<sub>2</sub>. For Ce/TiO<sub>2</sub>, two overlapping SO<sub>2</sub> desorption features were observed between 750 and 900 °C. The simultaneous desorption of O<sub>2</sub> with SO<sub>2</sub> suggests that these species were associated with sulfate decomposition. On the basis of previous studies,<sup>19,25</sup> we suggest that the low-temperature peak is associated with the decomposition of Ce(SO<sub>4</sub>)<sub>2</sub> and that the high-temperature peak is caused by the decomposition of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Therefore, the only desorption peak due to SO<sub>2</sub> observed on

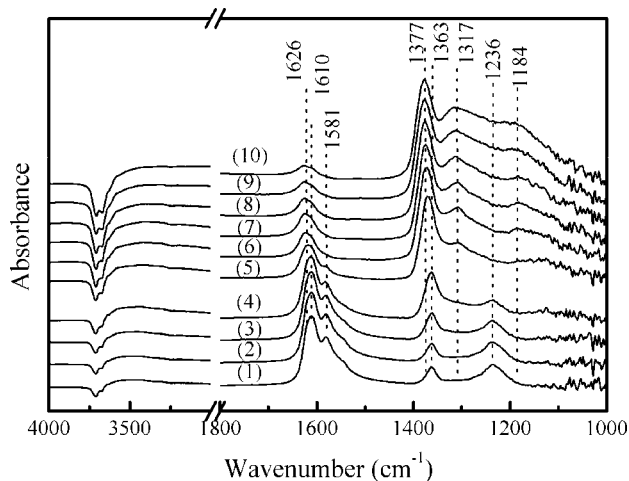


**Figure 7.** Changes of DRIFTS spectra of Ce/TiO<sub>2</sub> with time in a flow of SO<sub>2</sub> + O<sub>2</sub> at 300 °C (1–9) for 1, 3, 5, 10, 20, 30, 60, 120, and 180 min. (Reaction conditions: SO<sub>2</sub> 180 ppm, O<sub>2</sub> 5%, N<sub>2</sub> as balance.)

CeO<sub>2</sub> is assigned to Ce(SO<sub>4</sub>)<sub>2</sub> because Ce is in an oxidation state IV. In addition, the O<sub>2</sub> desorption on the CeO<sub>2</sub> and Ce/TiO<sub>2</sub> samples occurred before the onset of sulfate decomposition, which was due to the composition of bulk CeO<sub>2</sub>.

We also examined TPD experiments for fresh and poisoned Ce/TiO<sub>2</sub> samples by monitoring SO<sub>2</sub> ( $m/z = 64$ ) signal, as shown in Figure 6. For the S-1 h sample, most of the SO<sub>2</sub> was originated from the decomposition of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. As poisoning time increased, the signal ascribed to the decomposition of Ce(SO<sub>4</sub>)<sub>2</sub> emerged and increased. These results demonstrate that Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was more easily formed than Ce(SO<sub>4</sub>)<sub>2</sub> during the reaction of Ce/TiO<sub>2</sub> with SO<sub>2</sub> in the presence of O<sub>2</sub>. The present TPD results corroborate the XPS result and further support the idea that the sulfate species were formed on the catalyst, accompanied by the reduction of Ce(IV) to Ce(III). As discussed above, Ce is “locked” during the formation of high thermally stable sulfate and the redox cycle between Ce(IV) and Ce(III) is disrupted during the exposure to SO<sub>2</sub>.

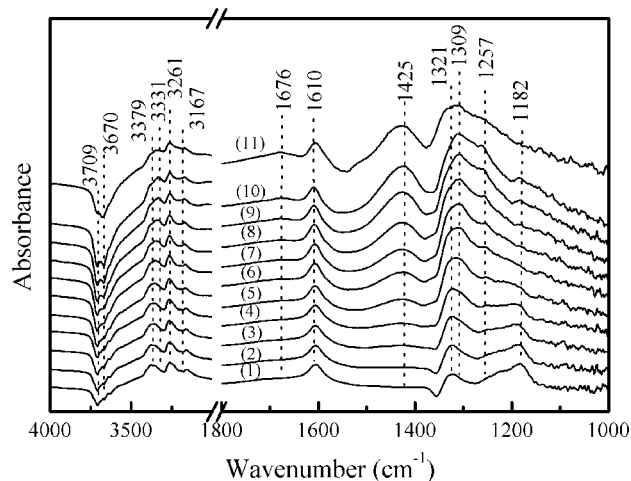
**DRIFT Studies.** As mentioned above, the chemical transformation of the active sites must be one of the reasons for the activity loss in the presence of SO<sub>2</sub>. To investigate the interaction between SO<sub>2</sub> and the reactants over the Ce/TiO<sub>2</sub> catalyst, we also conducted experiments using in situ DRIFTS. First, we investigated the interaction between SO<sub>2</sub> + O<sub>2</sub> and the catalyst to analyze the nature of the sulfate species on the Ce/TiO<sub>2</sub> catalyst. Figure 7 shows the DRIFTS spectra of Ce/TiO<sub>2</sub> as a function of exposure time in a flow of SO<sub>2</sub> + O<sub>2</sub> at 300 °C. After SO<sub>2</sub> + O<sub>2</sub> exposure, four peaks at 1626, 1363, 1309, and 1198 cm<sup>-1</sup> grew in intensity with time. According to other studies,<sup>26,27</sup> the peaks at 1363 and 1309 cm<sup>-1</sup> can be attributed to the surface sulfate species linked to different sites, such as Ce–Ce or Ce–Ti, whereas the band at 1198 cm<sup>-1</sup> can be attributed to the bulk sulfate species. The surface sulfate species band also underwent a blue shift (from 1363 to 1379 cm<sup>-1</sup>) with increasing coverage of the sulfate species on Ce/TiO<sub>2</sub>.<sup>28</sup> It should be noted that there was a drastic increase in the intensity of negative peaks at 3710 and 3672 cm<sup>-1</sup>, which were associated with the vibration of hydroxyl groups.<sup>29</sup> The consumption of surface OH species means that SO<sub>2</sub> was able to react with surface hydroxyl groups to form adsorbed H<sub>2</sub>O.<sup>30,31</sup> The synchronous growth of the band at 1626 cm<sup>-1</sup> and a broadband in the range of 3300–3500 cm<sup>-1</sup> in the spectra indicate that surface water was generated. Therefore, the band at 1626 cm<sup>-1</sup> is assigned to  $\delta_{\text{HOH}}$  of H<sub>2</sub>O.



**Figure 8.** DRIFTS spectra of Ce/TiO<sub>2</sub> in a flow of NO + O<sub>2</sub> before and after adding 180 ppm SO<sub>2</sub> at 300 °C. (1) Without SO<sub>2</sub> for 60 min. (2–10) Adding SO<sub>2</sub> for 1, 3, 5, 10, 20, 30, 60, 120, and 180 min. (Reaction conditions: NO 500 ppm, O<sub>2</sub> 5%, N<sub>2</sub> as balance.)

In principle, NO can be adsorbed in a molecular form and oxidized on oxide surfaces, giving rise to surface species such as NO<sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>2</sub>, and NO<sub>3</sub><sup>-</sup>, which were identified as key intermediates involved in SCR reactions.<sup>32–34</sup> Therefore, we investigated the effect of SO<sub>2</sub> on the oxidation of NO on the catalyst, and the results are shown in Figure 8. The bottom spectrum was obtained under a SO<sub>2</sub>-free flow, while the other spectra were obtained in the presence of 180 ppm SO<sub>2</sub> with different exposure times. After exposing Ce/TiO<sub>2</sub> to NO + O<sub>2</sub> for 60 min at 300 °C, four bands at 1610, 1581, 1363, and 1236 cm<sup>-1</sup> appeared, which were all due to the adsorbed nitrate species.<sup>35,36</sup> The addition of 180 ppm SO<sub>2</sub> in the feed for 10 min resulted in the appearance of a new surface sulfate species band at 1364 cm<sup>-1</sup>. This band shifted to 1377 cm<sup>-1</sup>, and its intensity increased sharply with exposure time. The sulfate species bands at 1317 and 1184 cm<sup>-1</sup>, together with the H<sub>2</sub>O band at 1626 cm<sup>-1</sup>, also appeared upon the introduction of SO<sub>2</sub> and increased with time. In contrast, obvious decreases were observed for the bands of the nitrate species. These results indicate that SO<sub>2</sub> has a significant inhibiting effect on the formation of nitrate.

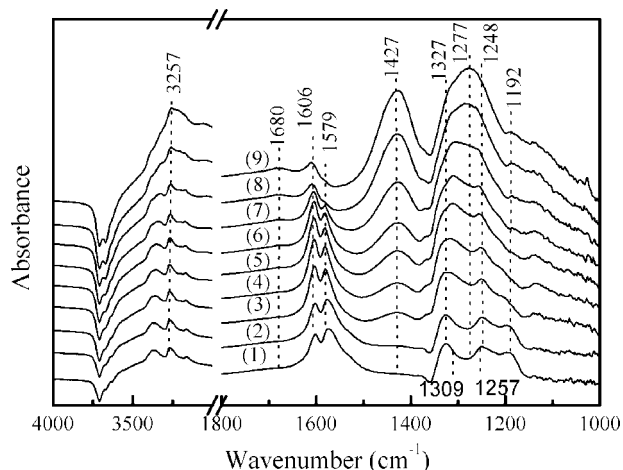
Figure 9 shows the effect of SO<sub>2</sub> on the oxidation of NH<sub>3</sub>. The bottom spectrum was obtained under a SO<sub>2</sub>-free flow. The exposure of the catalyst to a flow of NH<sub>3</sub> + O<sub>2</sub> at 300 °C for 60 min resulted in several bands. According to previous studies,<sup>37,38</sup> the bands at 1610 and 1182 cm<sup>-1</sup> could be attributed to the asymmetric and symmetric deformation modes of coordinated NH<sub>3</sub> on Lewis acid sites, respectively. Bands were also found at 3379, 3331, 3261, and 3167 cm<sup>-1</sup> in the NH stretching region. The band at 1321 cm<sup>-1</sup> could be due to the wagging mode of an amide species (NH<sub>2</sub>). Two negative bands at 3709 and 3670 cm<sup>-1</sup> were also found, which could be from the surface hydroxyl group. The introduction of 180 ppm SO<sub>2</sub> into the feed resulted in the appearance of several new bands at 1676, 1425, 1309, and 1257 cm<sup>-1</sup>. Their intensities increased with exposure time. The bands at 1676 and 1425 cm<sup>-1</sup> were likely due to the asymmetric and symmetric deformation modes of NH<sub>3</sub> coordinated on Brønsted acid sites (NH<sub>4</sub><sup>+</sup>).<sup>37,38</sup> Previous studies found that NH<sub>4</sub>HSO<sub>4</sub> was stable at 300 °C and started to decompose at about 390 °C,<sup>36</sup> compared to ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), which decomposed at 280 °C.<sup>14,39–42</sup> We deduce that NH<sub>4</sub>HSO<sub>4</sub> deposited on the surface of the catalyst during the reaction between NH<sub>3</sub> and SO<sub>2</sub> in the presence of O<sub>2</sub>.



**Figure 9.** DRIFTS spectra of Ce/TiO<sub>2</sub> in a flow of NH<sub>3</sub> + O<sub>2</sub> before and after adding 180 ppm SO<sub>2</sub> at 300 °C. (1) Without SO<sub>2</sub> for 60 min. (2–10) Adding SO<sub>2</sub> for 1, 3, 5, 10, 20, 30, 60, 120, and 180 min. (Reaction conditions: NH<sub>3</sub> 500 ppm, O<sub>2</sub> 5%, N<sub>2</sub> as balance.) (11) DRIFTS spectrum of NH<sub>4</sub>HSO<sub>4</sub>-deposited Ce/TiO<sub>2</sub> in a flow of N<sub>2</sub> at 300 °C.

Therefore, the bands at 1676 and 1425 cm<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> species originated from NH<sub>4</sub>HSO<sub>4</sub>, and their intensities increased with the accumulation of NH<sub>4</sub>HSO<sub>4</sub>. Moreover, the bands at 1309 and 1257 cm<sup>-1</sup>, which differed greatly from the bands at 1363 and 1309 cm<sup>-1</sup> for the sulfate species in Figure 7, were supposed to be associated with HSO<sub>4</sub><sup>-</sup> species that originated from NH<sub>4</sub>HSO<sub>4</sub>. To further examine the attribution of these bands, we examined the DRIFTS spectrum (the top spectrum in Figure 9) of the NH<sub>4</sub>HSO<sub>4</sub>-deposited catalyst exposed to N<sub>2</sub> at 300 °C, which was prepared by an impregnation method using a Ce/TiO<sub>2</sub> catalyst and an aqueous solution of NH<sub>4</sub>HSO<sub>4</sub>. As shown in Figure 9, the bands observed from the NH<sub>4</sub>HSO<sub>4</sub>-deposited catalyst were consistent with the results for the Ce/TiO<sub>2</sub> catalyst in a flow of NH<sub>3</sub> + O<sub>2</sub> after the addition of SO<sub>2</sub> for 180 min. It is demonstrated that NH<sub>4</sub>HSO<sub>4</sub> was formed on the surface of the Ce/TiO<sub>2</sub> catalyst by the reaction of SO<sub>2</sub> and NH<sub>3</sub> in the presence of O<sub>2</sub>.

To understand the deactivation mechanism of Ce/TiO<sub>2</sub> by SO<sub>2</sub> for the SCR of NO with NH<sub>3</sub>, the DRIFTS spectra of Ce/TiO<sub>2</sub> in a flow of NO + NH<sub>3</sub> + O<sub>2</sub> with and without SO<sub>2</sub> at 300 °C were recorded and are depicted in Figure 10. The reaction was initially carried out in a steady state flow of NO + NH<sub>3</sub> + O<sub>2</sub> maintained for 60 min followed by introduction of 180 ppm SO<sub>2</sub> into the feed. The bottom spectrum was obtained under a SO<sub>2</sub>-free flow, and the other spectra were obtained in the presence of 180 ppm SO<sub>2</sub> with different reaction times. Similarly, bands characteristic of the nitrate species (1606, 1579, and 1248 cm<sup>-1</sup>), NH, NH<sub>2</sub>, and NH<sub>3</sub> stretching related to NH<sub>3</sub> species (3150–3400, 1327, 1606, 1192 cm<sup>-1</sup>) appeared in a flow of NO + NH<sub>3</sub> + O<sub>2</sub> for 60 min. Several new bands appeared at 1680, 1427, 1309, and 1257 cm<sup>-1</sup> upon introduction of SO<sub>2</sub>. The bands at 1309 and 1257 cm<sup>-1</sup> associated with HSO<sub>4</sub><sup>-</sup> species were unclear because they overlapped adjacent peaks at 1327 (NH<sub>2</sub> species) and 1248 cm<sup>-1</sup> (nitrate species), respectively. Moreover, their intensities increased gradually with time. As a result, a combined band centered at 1277 cm<sup>-1</sup> was observed in Figure 10. The intensities of the bands at 1680 and 1427 cm<sup>-1</sup> due to NH<sub>4</sub><sup>+</sup> species also increased with time, which is consistent with the phenomena presented in Figure 9. In contrast, the bands for nitrate species promptly decreased with increasing SO<sub>2</sub> exposure time, while the bands attributed to NH



**Figure 10.** DRIFTS spectra of Ce/TiO<sub>2</sub> in a flow of NO + NH<sub>3</sub> + O<sub>2</sub> before and after adding 180 ppm SO<sub>2</sub> at 300 °C. (1) Without SO<sub>2</sub> for 60 min. (2–9) Adding SO<sub>2</sub> for 1, 5, 10, 20, 30, 60, 120, and 180 min. (Reaction conditions: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 5%, N<sub>2</sub> as balance.)

and NH<sub>3</sub> species remained almost unchanged. These results suggest that the addition of SO<sub>2</sub> not only inhibits the formation of nitrate but also results in the formation of NH<sub>4</sub>HSO<sub>4</sub> in the SCR reaction, which could deposit on the surface of the catalyst and block the active sites.

We observed that the effect of deposited NH<sub>4</sub>HSO<sub>4</sub> was crucial for the deactivation of the catalyst based on our DRIFTS results. However, there were no SO<sub>2</sub> desorption peaks starting around 390 °C in Figure 6, which could be ascribed to the decomposition of NH<sub>4</sub>HSO<sub>4</sub>. This may be associated with the different sensitivities of mass spectrometry (MS) and DRIFTS. DRIFTS is a surface-sensitive technology and only provides insight into the formation of surface NH<sub>4</sub>HSO<sub>4</sub>, while the species formed in the bulk phase cannot be detected. On the other hand, ammonia, which is one of the decomposition products of NH<sub>4</sub>HSO<sub>4</sub>, was undistinguishable from H<sub>2</sub>O by MS because they exhibited the same signal of  $m/z = 17$ . The other sulfate products may have been left on the surface of the samples and combined with Ce to form more stable Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. In that case, we would only have observed SO<sub>2</sub> as a decomposition product of Ce sulfate.

Combined with the activity results of the Ce/TiO<sub>2</sub> catalyst in Figure 1, we estimated that the decrease in NO conversion in the presence of SO<sub>2</sub> during the first 12 h was caused by the deposition of NH<sub>4</sub>HSO<sub>4</sub> on the surface of the Ce/TiO<sub>2</sub> catalyst, which could block the active sites of the catalyst and reduce its specific area. However, our results suggest that the formation of NH<sub>4</sub>HSO<sub>4</sub> is not the main deactivation route because of the limited sulfur coverage on the surface of the catalyst. The further decrease in NO conversion in the following 36 h was a result of a change in the catalyst. We theorize that the formation of Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is the primary reason for the permanent deactivation of the Ce/TiO<sub>2</sub> catalyst due to their high thermal stability. The formation of Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> disrupts the redox process between Ce(IV) and Ce(III), which is crucial for the adsorption and activation of reactants during the SCR reaction. Another factor affecting the deactivation is the inhibiting effect of sulfate on the formation and adsorption of the nitrate species, which is known to be one of the key intermediates during the SCR reaction, especially at low temperatures.

Furthermore, when the reaction temperature increased from 300 to 350 °C and the concentration level of SO<sub>2</sub> remained the

same, the negative effects from SO<sub>2</sub> were noticeably weaker. This suggests that at low temperatures, the SCR reaction over the Ce/TiO<sub>2</sub> catalyst may occur via the Langmuir–Hinshelwood mechanism since the activity decreased when the adsorption of nitrate was inhibited by the formative sulfate species. On the other hand, the SCR reaction may follow the Eley–Rideal mechanism at high temperatures because of the small association between the adsorbed nitrate species and the reaction activity. More detailed investigation of the SCR reaction mechanism over the Ce/TiO<sub>2</sub> catalyst will be conducted.

## Conclusions

The presence of SO<sub>2</sub> in the feed gas led to a permanent deactivation of the SCR of NO by NH<sub>3</sub> over the Ce/TiO<sub>2</sub> catalyst. The lower the reaction temperature the greater the negative effect of SO<sub>2</sub> was. In the presence of O<sub>2</sub>, NH<sub>3</sub> can easily react with SO<sub>2</sub> to favor the formation of NH<sub>4</sub>HSO<sub>4</sub>, which can deposit on the surface of the catalyst and block the active sites. The formative Ce(SO<sub>4</sub>)<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> on Ce/TiO<sub>2</sub> have high thermal stability and not only inhibit the formation of nitrate but also “lock” the cerium cation and disrupt the Ce(IV)/Ce(III) redox cycle. Both of these mechanisms are necessary for the SCR reaction. This is shown to be the primary reason for the deactivation of the Ce/TiO<sub>2</sub> catalyst during the SCR of NO by NH<sub>3</sub> in the presence of SO<sub>2</sub>. Therefore, we conclude that the Ce/TiO<sub>2</sub> catalyst is only suitable for practical applications in sulfur-free or low-sulfur gas streams. The addition of other promoters to inhibit the oxidation of SO<sub>2</sub> to form sulfate should be considered for further improvement of sulfur tolerance using this type of catalyst.

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## References and Notes

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