Effect of SO$_2$ on the Selective Catalytic Reduction of NO$_x$ over V$_2$O$_5$-CeO$_2$/TiO$_2$-ZrO$_2$ Catalysts

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Abstract: The effect of SO$_2$ on the selective catalytic reduction of NO$_x$ by NH$_3$ over V$_2$O$_5$-0.2CeO$_2$/TiO$_2$-ZrO$_2$ catalysts was studied through catalytic activity tests and various characterization methods, like Brunner–Emmet–Teller (BET) surface measurement, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray fluorescence (XRF), hydrogen temperature-programmed desorption (H$_2$-TPR), X-ray photoelectron spectroscopy (XPS) and in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS). The results showed that the catalyst exhibited superior SO$_2$ resistance when the volume fraction of SO$_2$ was below 0.02%. As the SO$_2$ concentration further increased, the NO$_x$ conversion exhibited some degree of decline but could restore to the original level when stopping feeding SO$_2$. The deactivation of the catalyst caused by water in the flue gas was reversible. However, when 10% H$_2$O was introduced together with 0.06% SO$_2$, the NO$_x$ conversion was rapidly reduced and became unrecoverable. Characterizations indicated that the specific surface area of the deactivated catalyst was significantly reduced and the redox ability was weakened, which was highly responsible for the decrease of the catalytic activity. XPS results showed that more Ce$^{3+}$ was generated in the case of reacting with SO$_2$. In situ DRIFTS results confirmed that the adsorption capacity of SO$_2$ was enhanced obviously in the presence of O$_2$, while the SO$_2$ considerably refrained the adsorption of NH$_3$. The adsorption of NO$_x$ was strengthened by SO$_2$ to some extent. In addition, NH$_3$ adsorption was improved after pre-adsorbed by SO$_2$ + O$_2$, indicating that the Ce$^{3+}$ and more oxygen vacancy were produced.

Keywords: V$_2$O$_5$-CeO$_2$/TiO$_2$-ZrO$_2$; selective catalyst reduction; catalyst; in situ DRIFTS; SO$_2$

1. Introduction

Selective catalytic reduction (SCR) catalysts are commonly severely deactivated by SO$_2$, which is abundantly present in flue gas. There are two mechanisms that can explain the sulfur poisoning of catalysts. Firstly, SO$_2$ reacts with NH$_3$ and vapor in the oxygen atmosphere, producing sulfate species including ammonium sulfate and ammonium bisulfate. These sulfate substances can deposit on the catalytic surface and cause pore plugging. As a result, the specific surface area and pore volume decrease observably, ending up with the catalyst deactivation. Studies have shown that the thermal decomposition temperature range of ammonium sulfate and ammonium bisulfate are 213–308 °C and 308–419 °C [1], respectively. It is still hard for these sulfate species to decompose over a traditional V/TiO$_2$ catalyst. In the second, SO$_2$ can react with the active center atoms and produce metal sulfates, which will decrease catalyst activity [2,3]. The former deactivation is reversible and the catalysts can be reactivated by washing and high-temperature processing. However, the later deactivation is irreversible.

The mechanism of catalyst sulfur poisoning has been extensively studied. Wei et al. [4] claimed that SO$_2$ significantly reduced the adsorption of NH$_3$ on the Lewis acid sites. At the same time, SO$_2$
would react with NH$_4^+$ to form NH$_4$HSO$_3$, thereby reducing NO$_x$ conversion. However, Jiang et al. [5] proposed that SO$_2$ had little effect on the adsorption of NH$_3$, and conversely, promoted the formation of new Bronsted acid sites. The weakening of NO adsorption on the catalyst surface was the main cause of deactivation. With the deposition of sulfate on the catalyst surface, less NO participated in the SCR reaction, resulting in a decrease in NO$_x$ conversion. Similarly, Liu et al. [6] claimed that SO$_2$ had a significant inhibitory effect on the reduction of NO$_x$ due to the deposition of sulfate substances. It hindered the adsorption of NO and the production of the intermediate ammonium nitrate, resulting in a decrease in catalyst activity. Moreover, Pan et al. [7] found that the main reason for MnO$_x$/TiO$_2$ catalysts deactivation was that the active center atom manganese was sulfated. Besides, the presence of SO$_2$ caused ammonium sulfate to deposit on the catalyst, decreasing the adsorption of NO. Gu et al. [8] reported that the main reason for the deactivation of Ce/TiO$_2$ catalyst was that SO$_2$ could react with the catalyst to form high thermally stable Ce(SO$_4$)$_2$ and Ce$_2$(SO$_4$)$_3$, and Xu et al. obtained similar results [9].

On the basis of the above literatures, it is found that there are still many controversies about the mechanism of catalyst sulfur poisoning. Moreover, there is no report found currently on the sulfur poisoning mechanism of V$_2$O$_5$-CeO$_2$/TiO$_2$-ZrO$_2$ catalysts, which were reported to be an excellent SCR catalyst with a wide temperature range [10–12]. Our previous studies indicated that the V$_2$O$_5$-0.2CeO$_2$/TiO$_2$-ZrO$_2$ catalyst exhibited superior catalytic performance as well as high tolerance of SO$_2$ and H$_2$O. In this paper, the catalytic activity of V$_2$O$_5$-0.2CeO$_2$/TiO$_2$-ZrO$_2$ in the presence of different SO$_2$ content was further studied. Various characterization methods such as the Brunner–Emmet–Teller (BET) surface measurement, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray fluorescence (XRF), hydrogen temperature-programmed desorption (H$_2$-TPR), X-ray photoelectron spectroscopy (XPS) and in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) were employed to study the poisoning mechanism from a microscopic aspect.

2. Materials and Methods

2.1. Catalyst Preparation

The Ti–Zr carrier was prepared by a coprecipitation method with the molar ratio of Ti:Zr = 1:1. An equal amount of TiCl$_4$ solution and ZrOCl$_2$ 8H$_2$O were dissolved in deionized water and stirred constantly. With stirring, NH$_3$·H$_2$O was slowly added until the pH reached 10. The obtained solution was aged at room temperature for 24 h. Then, the precipitate was washed with deionized water until the supernatant contained no Cl$^-$ . Finally, the sample was dried at 110 °C for 12 h and then calcined at 450 °C for 4 h in a muffle furnace.

A step-by-step impregnation method was used to prepare V$_2$O$_5$-0.2CeO$_2$/TiO$_2$-ZrO$_2$. A certain amount of Ce(NO$_3$)$_3$·6H$_2$O and Ti–Zr powder were added to deionized water. The obtained suspension was stirred at room temperature for 2 h, followed by stirred at 85 °C for 4 h. After dried at 110 °C for 12 h and calcined in a muffle furnace at 450 °C for 4 h, the Ce/Ti–Zr sample was obtained. Thereafter, the resulting Ce/Ti–Zr was impregnated with NH$_4$VO$_3$ solution in the same manner. The obtained sample was denoted as V-0.2Ce/Ti–Zr, where the content of V$_2$O$_5$ loading was 1 wt. % and the molar ratio of Ce to Ti–Zr support = 0.2.

For short, the V-0.2Ce/Ti–Zr catalyst after reaction with 0.06% SO$_2$ for 2 h was denoted as S-V-0.2Ce/Ti–Zr, while the catalyst after reaction with 10 vol% H$_2$O and 0.06% SO$_2$ for 2 h was denoted as HS-V-0.2Ce/Ti–Zr, respectively.

2.2. Activity Measurements

The SCR activity measurement of catalysts was carried out in a fixed-bed reactor with the inner diameter of 7 mm. The 0.3 g catalyst (40–60 mesh) was placed in the reactor with a gas hourly space velocity (GHSV) of 20000 h$^{-1}$. Typically, the total gas flow was 100 mL/min. The simulated gas was composed of 0.08% NO, 0.08% NH$_3$, 5% O$_2$, 5%/10% H$_2$O (when used), 0.02%/0.04%/0.06% SO$_2$ (when
used) and N₂ as the balanced gas. The NO, NO₂ and NOₓ concentration were persistently monitored with a flue gas analyzer (Testo350-XL).

2.3. Catalyst Characterization

The BET was measured using a specific surface area and pore size analyzer V-Sorb 2800P (Beijing Gold APP, Beijing, China). The sample was pretreated under vacuum at 250 °C for 5 h, and the adsorbate was high purity nitrogen.

XRD patterns were carried out for phase analysis via a SmartLab™ X-ray diffractometer (Rigaku, Tokyo, Japan). Cu target acted as the X-ray source.

The morphology of the catalyst was determined by TEM (Thermo Fisher Scientific, Waltham, Massachusetts, America). The catalyst sample was dispersed in an ethanol solution after thoroughly ground, followed by shaken under ultrasonic waves for 15 min.

XRF spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, MA, America) was used to analyze the content of component in the catalyst sample.

H₂-TPR was carried out in a quartz U-tube reactor connected to a thermal conduction detector (TCD) using an H₂–Ar mixture (10% H₂ by volume) as reductant (Finetec Instruments, Hangzhou, Zhejiang, China). The temperature range during the test was for 25 °C to 800 °C with a heating rate of 10 °C/min.

XPS analysis was performed on a PHI Quantera II system (Ulvac-PHI, Chigasaki, Kanagawa Prefecture, Japan). The binding energies were referenced to the C 1 s line at 284.8 eV from adventitious carbon.

In situ DRIFTS studies were performed on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, MA, USA). The scanning wave number ranged from 400 cm⁻¹ to 4000 cm⁻¹. Before the test, the sample was pretreated with N₂ at 400 °C for 1 h to remove impurities. The background at a certain temperature was collected during the cooling process.

3. Results and Discussion

3.1. Effects of SO₂ and H₂O on Catalyst Activity

Figure 1 showed the catalytic activity results with different concentration SO₂ over the V-0.2Ce/Ti–Zr catalyst at 250 °C. In the absence of SO₂, NOₓ conversion of the V-0.2Ce/Ti–Zr catalyst was approximately 90%, indicating that the catalyst had high activity at the low temperature. After 0.02% SO₂ was introduced, NOₓ conversion remained stable. However, NOₓ conversion decreased rapidly to 71% and 65% at 20 min respectively when 0.04% and 0.06% SO₂ were added. Furthermore, it could be found that the catalytic activity could recover after stopping SO₂. It was inferred that SO₂ and SO₃ reacted with NH₃ in the early stage, leading to the decrease of NH₃ as well as the catalytic performance. As the reaction went on, SO₂ and SO₃ reacted with CeO₂ and produced Ce³⁺ in the presence of excess oxygen, which could strengthen the acid sites on the catalyst and increased NOₓ conversion [13].

The effect of H₂O on the catalytic activity of the catalyst was investigated and the results were shown in Figure 2. It was found that the activity of the catalyst was rapidly decreased with the introduction of H₂O. However, after the H₂O was stopped, the activity gradually recovered almost to the original level, thus indicating that the effect of H₂O on the catalyst was reversible.

The activity of the V-0.2Ce/Ti–Zr catalyst was tested at 250 °C in the presence of 10% H₂O and different concentrations of SO₂, and the results were shown in Figure 3. After the introduction of SO₂ and H₂O, NOₓ conversion decreased rapidly to less than 30%, which was much lower than that in the presence of SO₂ or H₂O alone. After SO₂ and H₂O were removed, NOₓ conversion increased to some extent but could not be restored to the initial level, indicating an irreversible deactivation occurred. Studies showed that SO₂ would react with NH₃ to form ammonium sulfates, and block active sites on the surface of the catalyst.
Figure 1. NO\textsubscript{x} conversion of V-0.2Ce/Ti–Zr in the presence of SO\textsubscript{2} (250 °C). Reaction condition: NH\textsubscript{3} = NO = 0.08\%, O\textsubscript{2} = 5\%, N\textsubscript{2} as balance, SO\textsubscript{2} content: 0.02\%, 0.04\% and 0.06\%, all by volume.

Figure 2. NO\textsubscript{x} conversion of V-0.2Ce/Ti–Zr in the presence of H\textsubscript{2}O (250 °C).

Figure 3. NO\textsubscript{x} conversion of V-0.2Ce/Ti–Zr in the presence of H\textsubscript{2}O and SO\textsubscript{2} (250 °C; reaction condition: NH\textsubscript{3} = NO = 0.08\%, O\textsubscript{2} = 5\%, H\textsubscript{2}O = 10\%, SO\textsubscript{2} = 0.02\%, 0.04\% and 0.06\%, all by volume).

Furthermore, the performance of the HS-V-0.2Ce/Ti–Zr catalyst at different temperatures was also tested, and the results were shown in Figure 4. It could be found that the mid-temperature (200–300 °C) activity of the HS-V-0.2Ce/Ti–Zr catalyst was significantly decreased, while it at a higher temperature (>300 °C) was obviously enhanced. One literature indicated that the formation of Ce(SO\textsubscript{4})\textsubscript{2} led to a
decrease in the activity of the catalyst at moderate temperatures [14]. At the same time, Xu et al. [15] pointed out that the sulphate was produced during the poisoning process, which had a certain activity at high temperatures and could improve the high temperature activity of the catalyst.

![Figure 4](image)

**Figure 4.** NOx conversion of the V-0.2Ce/Ti–Zr and HS-V-0.2Ce/Ti–Zr catalyst.

### 3.2. Physico-Chemical Characterization of Catalysts

#### 3.2.1. BET Analysis

The specific surface area of the catalysts before and after being poisoned by SO2 was illustrated in Table 1. Compared with the fresh sample, the BET surface area of the S-V-0.2Ce/Ti–Zr catalyst decreased from 54.45 m²/g to 25.07 m²/g, and that of the HS-V-0.2Ce/Ti–Zr catalyst further reduced to 15.27 m²/g. While with comparison to the fresh counterpart, there was no apparent change on the pore volume. The specific surface area of the catalyst was related to the adsorption capacity of NH3 during the SCR reaction, thereby further affecting the denitrification activity.

| Sample           | BET Surface Area (m²/g) | Pore Volume (mL/g) |
|------------------|-------------------------|--------------------|
| V-0.2Ce/Ti–Zr    | 54.45                   | 0.14               |
| S-V-0.2Ce/Ti–Zr  | 25.07                   | 0.16               |
| HS-V-0.2Ce/Ti–Zr | 15.27                   | 0.11               |

In order to further investigate the reason for the significant decrease in the BET specific surface area, the pore size distribution of the catalyst was mapped. As shown in Figure 5, the pore size range of the fresh catalyst was mainly concentrated at 2 nm to 10 nm, indicating that the mesopores contributed the most to the specific surface area of the catalyst. For the catalyst after reaction with O2, the number of macropores and mesopores (in the range of 5.3 nm to 50 nm) increased, and the increase of pore diameter in HS-V-0.2Ce/Ti–Zr catalyst was more pronounced. It was found that the mesopores (mainly 2 nm to 10 nm) contributed the most to the specific surface area of the catalyst. Therefore, it was presumed that the number of mesopores determined the NH3-SCR activity of the V-0.2Ce/Ti–Zr catalyst. After the reaction in presence of H2O and SO2, mesopores in the range of 5–50 nm contributed greatly to the specific surface area of the catalyst, while the mesopores and micropores with pore diameters less than 5 nm gradually decreased. Based on the above analysis, it was speculated that in the presence of SO2 and H2O, (NH4)2SO4 and Ce(SO4)2 formed during the reaction were adsorbed on the catalyst, and blocked 2 to 5 nm mesopores and micropores around the active component of the catalyst. These caused a decrease in specific surface area of the catalyst, further inhibiting catalytic activity.
3.2.2. XRD Analysis

To further study the microstructure of the poisoned V-0.2Ce/Ti–Zr, an XRD analysis was performed. As shown in Figure 6, catalysts before and after being poisoned by SO₂ showed similar spectra. According to our previous research [12], these diffraction peaks mainly corresponded to ZrTiO₂, ZrO₂, V₂O₅, CeO₂ and TiO₂. Diffraction peaks of substances such as (NH₄)₂SO₄ or Ce(SO₄)₂ were not detected. The results illustrated that no sulphate with good crystal form was formed, or the amount of sulphate formed on the surface was small and highly dispersed.
was detected in the S-V-0.2Ce/Ti–Zr catalyst, while a trace amount of the S element was detected in the HS-V-0.2Ce/Ti–Zr catalyst. The results revealed that when SO$_2$ was separately introduced, substantially no S element was present on the catalyst surface, or its content was extremely low. However, once H$_2$O was introduced together, SO$_2$ was more likely to participate in the reaction, and was present on the surface in the form of ammonium sulfate or Ce(SO$_4$)$_2$.

Figure 6. XRD patterns of the catalysts (a) V-0.2Ce/Ti–Zr, (b) S-V-0.2Ce/Ti–Zr and (c) HS-V-0.2Ce/Ti–Zr.

3.2.3. TEM and XRF Analysis

TEM was carried out to study the morphology changes of catalysts poisoned by H$_2$O and SO$_2$. As shown in Figure 7, the surface of the fresh catalyst was uniform and had a good dispersion. While for the poisoned one, it was clearly observed that the surface was covered with some substances, and the particles were agglomerate.

Figure 7. TEM pictures of the catalysts before and after poisoning by SO$_2$. (a) V-0.2Ce/Ti–Zr and (b) HS-V-0.2Ce/Ti–Zr.

Element content of the catalyst was tested and the results were shown in Table 2. No S element was detected in the S-V-0.2Ce/Ti–Zr catalyst, while a trace amount of the S element was detected in the HS-V-0.2Ce/Ti–Zr catalyst. The results revealed that when SO$_2$ was separately introduced, substantially no S element was present on the catalyst surface, or its content was extremely low. However, once H$_2$O was introduced together, SO$_2$ was more likely to participate in the reaction, and was present on the surface in the form of ammonium sulfate or Ce(SO$_4$)$_2$. 

Table 2. XRF results of the catalysts before and after being poisoned by SO$_2$. 

| Sample          | V  | Ce | Ti | Zr | S  |
|-----------------|----|----|----|----|----|
| V-0.2Ce/Ti–Zr   | 0.723 | 12.512 | 1.2 | 34.66 | 0  |
| HS-V-0.2Ce/Ti–Zr |     |    |    |    |    |
work, peaks centered at 343 °C and 580 °C were due to the reduction of vanadium from V5+ to V4+ and V4+ to V3+, respectively. The reduction peak centered at 418 °C was attributed to the surface (α) reduction of CeO2, and the subsurface layers and deeper regions of the catalyst nanoparticles were reduced at 507 °C. It could be found that the redox ability of the S-V-0.2Ce/Ti–Zr catalyst was significantly weakened, according to the fact that several peaks disappeared (343 °C, 418 °C and 580 °C). After reaction with SO2 and H2O, the redox ability of the HS-V-0.2Ce/Ti–Zr catalyst was further attenuated, and only one reduction peak appeared at 458 °C was detected. Peaks centered at 495 °C and 458 °C were due to the reduction of Ce4+, while the peak at 653 °C was attributed to the reduction of V5+ to V3+ and the reduction of bulk phase Ce4+. It could be found that the disappearance of reduction peaks related with vanadium was an important cause of catalytic deactivation. For S-V-0.2Ce/Ti–Zr sample, the α-reduction peak of Ce4+ disappeared, which should be related to the reduction of Ce4+ to Ce3+. It was reported that the concentration of Ce3+ was used to assess the amount of oxygen formed. The oxygen vacancies were driven by the transition from Ce4+ to Ce3+, accelerating the transport of active oxygen species and facilitating the reaction vacancies, which could explain the phenomenon that the activity of the catalyst decreased first and then gradually increased. After being poisoned by SO2 and H2O, the intensity of the β reduction peak (458 °C) was significantly weakened, and the reduction peak of the vanadium oxide completely disappeared. It was speculated that the formed ammonium

### Table 2. XRF results of the catalysts before and after being poisoned by SO2.

| Sample         | V   | Ce  | Ti  | Zr  | S   |
|----------------|-----|-----|-----|-----|-----|
| V-0.2Ce/Ti–Zr  | 0.723 | 12.512 | 1.2  | 34.66 | 0   |
| S-V-0.2Ce/Ti–Zr | 0.63  | 12.365 | 19.75 | 26.66 | 0   |
| HS-V-0.2Ce/Ti–Zr | 0.558 | 12.932 | 20.46 | 26.4  | 1.13|

3.2.4. H2-TPR Analysis

TPR profiles for catalysts before and after poisoned by SO2 were presented in Figure 8. For the fresh catalyst, five reduction peaks were observed at 343 °C, 418 °C, 507 °C, 580 °C and 732 °C, respectively. Studies have shown that the low temperature reduction of V/TiO2 catalyst is mainly related to the monomer vanadium or highly dispersed vanadium species [16]. Held et al. proposed that the reduction peak at about 730 °C was mainly related to V2O4 [17]. Based upon our previous work, peaks centered at 343 °C and 580 °C were due to the reduction of vanadium from V5+ to V4+ and V4+ to V3+, respectively. The reduction peak centered at 418 °C was attributed to the surface (α) reduction process of CeO2, and the subsurface layers and deeper regions of the catalyst nanoparticles were reduced at 507 °C.

![Figure 8. Hydrogen temperature-programmed desorption (H2-TPR) patterns of the catalysts before and after being poisoned by SO2. (a) V-0.2Ce/Ti–Zr, (b) S-V-0.2Ce/Ti–Zr and (c) HS-V-0.2Ce/Ti–Zr.](image-url)
hydrogen sulfate was deposited on the surface of the catalyst or more stable Ce\(_2\)(SO\(_4\))\(_3\) was formed, which hindered the conversion of vanadium active species and led to a reduction of the redox ability.

3.2.5. XPS Analysis

Figure 9a showed the XPS results of Ce 3d. Peaks u''', u''', u and v''', v' can be corresponded to Ce\(^{4+}\), while peaks u' and v' were assigned to Ce\(^{3+}\), respectively. It can be seen from Figure 9a that Ce in the catalyst mainly existed in the Ce\(^{4+}\) valence state. As shown in Table 3, after reacting with 0.06% SO\(_2\) for 2 h, the ratio of Ce\(^{3+}\)/(Ce\(^{4+}\)+Ce\(^{3+}\)) in S-V-0.2Ce/Ti–Zr catalysts was increased to 25.15% compared with that in V-0.2Ce/Ti–Zr (24.94%), indicating more Ce\(^{3+}\) was generated. However, in the presence of SO\(_2\) and H\(_2\)O, the ratio of Ce\(^{3+}\)/(Ce\(^{4+}\)+Ce\(^{3+}\)) was reduced again to 24.93%. Hence, it was deduced that the introduction of SO\(_2\) promoted the conversion of Ce\(^{4+}\) and Ce\(^{3+}\), while the formed ammonium hydrogen sulfate on the surface of the catalyst could block the path of mutual conversion between Ce\(^{4+}\) and Ce\(^{3+}\).

![Ce 3d XPS spectra](image)

![O 1s XPS spectra](image)

**Figure 9.** XPS spectra of Ce 3d and O 1s on catalysts before and after being poisoned by SO\(_2\). (a) V-0.2Ce/Ti–Zr; (b) S-V-0.2Ce/Ti–Zr and (c) HS-V-0.2Ce/Ti–Zr.
As shown in Figure 9b, the three peaks in O 1 s can be assigned to oxygen vacancy, adsorbed oxygen and oxygen lattice from higher binding energy to lower binding energy. The adsorbed oxygen and oxygen lattice were marked as $O^\alpha$ and $O^\beta$, respectively [18,19]. The oxygen vacancy was formed due to the evolution of the oxygen lattice [20].

As can be seen in Table 3, the ratio of $O^\beta/(O^\alpha + O^\beta)$ was reduced significantly in the S-V-0.2Ce/Ti–Zr catalysts and even worse in the HS-V-0.2Ce/Ti–Zr catalysts. The existence of $O^\beta$ could promote the oxidation of NO to NO$_2$, which can explain the decrease in activity of the catalysts poisoned by SO$_2$.

### 3.3. In Situ DRIFTS Study

#### 3.3.1. Sulfur Dioxide Adsorption

Figure 10 showed the DRIFTS spectra of the V-0.2Ce/Ti–Zr catalyst in the flow of 0.06% SO$_2$ at 50 °C and then purged by N$_2$ with increasing temperatures from 50 °C to 400 °C. The peak at 1633 cm$^{-1}$ was linked to H$_2$O vibration produced by the reaction of SO$_2$ and hydroxyl on the catalytic surface [8]. With the addition of SO$_2$ at 50 °C, peaks at 1376 cm$^{-1}$, 1338 cm$^{-1}$, 1265 cm$^{-1}$, 1097 cm$^{-1}$ and 1049 cm$^{-1}$ were detected. Based on the research of Peak et al. [21], the triply degenerate asymmetric stretching $\nu_3$ band were accessible to FTIR investigation, and would split into three bands when the bidentate sulfate complex was formed. Therefore, it was deduced that the bands at 1265 cm$^{-1}$, 1097 cm$^{-1}$ and 1049 cm$^{-1}$ were attributed to bidentate sulfate on V-0.2Ce/Ti–Zr. The band at 1338 cm$^{-1}$ was assigned to the adsorbed SO$_2$, which mainly exists in the form of SO$_4^{2-}$. The band at 1376 cm$^{-1}$ might be due to the asymmetric vibration of O-S=O covalent groups (SO$_4^{2-}$). When the temperature reached 100 °C, the adsorption peak at 1376 cm$^{-1}$ disappeared [22,23].

Figure 10. In situ DRIFTS spectra of V-0.2Ce/Ti–Zr treated in flowing 0.06% SO$_2$ at 50 °C and then purged by N$_2$ at a different temperature.

Figure 11a shows the in situ DRIFTS spectra of the V-0.2Ce/Ti–Zr catalyst in the flow of 0.06% SO$_2$ at 250 °C and then purged with N$_2$. After adding SO$_2$ for 5 min, bands at 1363 cm$^{-1}$, 1344 cm$^{-1}$, 1295 cm$^{-1}$, 1083 cm$^{-1}$ and 1047 cm$^{-1}$ were detected with increasing intensity. The bands at 1295 cm$^{-1}$, 1107 cm$^{-1}$ and 1050 cm$^{-1}$ were contributed to the bidentate sulfate on V-0.2Ce/Ti–Zr while the band at

| Sample               | $\frac{Ce^{4+}}{Ce^{3+}+Ce^{4+}}$ | $\frac{O_e}{O_f+O_e}$ |
|----------------------|---------------------------------|-----------------------|
| V-0.2Ce/Ti–Zr        | 24.94                           | 28.14                 |
| S-V-0.2Ce/Ti–Zr      | 25.15                           | 20.71                 |
| HS-V-0.2Ce/Ti–Zr     | 24.93                           | 18.67                 |

Table 3. Peak area ratio of XPS.
1344 cm$^{-1}$ was assigned to the adsorbed SO$_2$ (SO$_3^{2-}$). The band at 1363 cm$^{-1}$ could be attributed to the asymmetric vibration of O = S = O covalent groups (SO$_4^{2-}$). It had been found that the O = S = O asymmetric covalent groups arose from the VOSO$_4$ adsorption peak that appeared at 1383 cm$^{-1}$ [24,25]. Hence, we deduced the reaction between the adsorbed SO$_2$ with V$_2$O$_5$ in the catalyst to form the VOSO$_4$ intermediate.

![Figure 11a](image1.png)

![Figure 11b](image2.png)

**Figure 11.** In situ DRIFTS spectra recorded at 250 °C in a flow of 0.06% SO$_2$ and 0.06% SO$_2$ + 5% O$_2$ over V-0.2Ce/Ti–Zr. (a) SO$_2$ adsorption and (b) SO$_2$ + O$_2$ co-adsorption.

Figure 11b shows the DRIFTS spectra of the V-0.2Ce/Ti–Zr catalyst in the flow of O$_2$ + SO$_2$ at 250 °C and then purged with N$_2$. In general, catalysts exhibited similar peaks, while the intensity of SO$_2$ adsorption was enhanced significantly in the presence of O$_2$.

### 3.3.2. Effect of SO$_2$ on NH$_3$ Adsorption

Figure 12 showed the NH$_3$ adsorption results on V-0.2Ce/Ti–Zr in the presence of SO$_2$. It could be found that original adsorption capacity of NH$_3$ was very weak, and only the band at 1182 cm$^{-1}$ was observed [26]. Then NH$_3$ was switched off and SO$_2$ + O$_2$ was introduced. The NH$_3$ adsorption peak was replaced by SO$_3^{2-}$ adsorption peak quickly. Bands at 1278 cm$^{-1}$, 1178 cm$^{-1}$ and 1050 cm$^{-1}$ were assigned to SO$_3^{2-}$ three-fold degeneracy asymmetric stretching vibration $v_3$ and the band at 1340 cm$^{-1}$ was assigned to the adsorbed SO$_2$ while the band at 1373 cm$^{-1}$ could be attributed to the asymmetric vibration of O = S = O covalent groups (SO$_4^{2-}$).

![Figure 12](image3.png)

**Figure 12.** In situ DRIFTS spectra of V-0.2Ce/Ti–Zr pretreated by NH$_3$ exposed to NH$_3$ + SO$_2$ + O$_2$ for various times.
In Figure 13, the catalysts were pretreated by 0.06% SO₂ + O₂ for 30 min, and then exposed to 800 ppm NH₃, followed by treating with SO₂ and O₂ again. After adding NH₃, several bands at 1660 cm⁻¹, 1600 cm⁻¹, 1440 cm⁻¹ and 1220 cm⁻¹ were detected. The band at 1600 cm⁻¹ and 1220 cm⁻¹ was associated with the asymmetric and symmetric deformation vibration of NH₃ adsorbed on Lewis acid sites, while the band at 1660 cm⁻¹ and 1440 cm⁻¹ were due to the asymmetric and symmetric deformation of NH₄⁺ bound to Brønsted acid sites [26,27]. Compared with the results of Figure 9, it could be found that the intensity of bands due to adsorbed NH₃ was significantly increased after being pretreated by SO₂ and O₂. It was deduced that the presence of SO₂ and O₂ could promote the transformation from Ce⁴⁺ to Ce³⁺ (the formation of Ce₂(SO₄)(SO₃)), resulting in the enhancement of the NH₃ adsorption ability. Furthermore, it was observed that the intensity of the NH₃ adsorption peaks did not change significantly after the introduction of SO₂ and O₂ again.

![Figure 13](image-url)  
**Figure 13.** In situ DRIFTs spectra of V-0.2Ce/Ti–Zr pretreated by SO₂ + O₂ exposed to NH₃ for various times and then treated by SO₂ + O₂ again.

3.3.3. Effect of SO₂ on NO Adsorption

The competitive adsorption behavior of SO₂ with NO₂ in the presence of O₂ was investigated, and in situ DRIFTS results were shown in Figure 14. As shown in Figure 15, bands appeared at 1375 cm⁻¹ and 1315 cm⁻¹ were due to cis-N₂O₂²⁻, and it could be found that the intensity of the bands increased gradually and the purge of N₂ had little influence on the adsorption bands. Band at 1190 cm⁻¹ were attributed to the bridging nitrates [28]. After 10 min, SO₄²⁻ adsorption peak appeared at 1046 cm⁻¹. As the reaction went on, it divided into two adsorption peaks (1049 cm⁻¹ and 1035 cm⁻¹). Along with the purge of N₂, band at 1095 cm⁻¹ assigned to bidentate sulfate was observed. Furthermore, weak SO₄²⁻ adsorption band was detected at 1135 cm⁻¹.

![Figure 14](image-url)  
**Figure 14.** In situ DRIFTs spectra taken at 250 °C in a flow of 0.08% NO + 0.06% SO₂ + 5% O₂ on V-0.2Ce/Ti–Zr.
Various times, followed by NO adsorption on the catalyst surface. In addition, our previous research has a certified catalyst that strengthened and the purge of NO adsorption bands at 1280 cm$^{-1}$.

The band at 1373 cm$^{-1}$ could be attributed to the asymmetric vibration of O = S = O covalent groups and bands at 1043 cm$^{-1}$ were detected. The band at 1188 cm$^{-1}$ was assigned to the adsorbed NO species.

As shown in Figure 15, bands due to the cis-N$_2$O$_2^{2-}$ were also detected at 1375 cm$^{-1}$ and 1315 cm$^{-1}$. Band at 1188 cm$^{-1}$ was assigned to the adsorbed NO$_x$ species. Nitrate species adsorption peak appeared at 1144 cm$^{-1}$ and 1067 cm$^{-1}$ after NO + O$_2$ pre-adsorption. Once feeding SO$_2$, the intensity of the bands at 1375 cm$^{-1}$, 1315 cm$^{-1}$, 1188 cm$^{-1}$ and 1144 cm$^{-1}$ were strengthened and the purge of N$_2$ had little influence on the adsorption bands, while the band at 1067 cm$^{-1}$ gradually disappeared. The SO$_4^{2-}$ adsorption peak appeared at 1046 cm$^{-1}$.

Based on the analysis above, it could be concluded that the presence of SO$_2$ could promote NO adsorption on the catalyst surface. In addition, our previous research has a certified catalyst that mainly follows the Eley–Rideal (E-R) mechanism, and NO adsorption on the catalyst surface restraints the SCR reaction [12]. Thus, it can explain the decrease of catalyst activity when SO$_2$ was injected.

3.3.4. Effect of SO$_2$ on NH$_3$ + NO + O$_2$ Co-Adsorption

As shown in Figure 16, in the presence of NH$_3$ + NO + O$_2$, only the band at 1205 cm$^{-1}$ due to adsorbed NH$_3$ was observed. After 0.06% SO$_2$ was injected, adsorption intensity of bands due to adsorbed NH$_3$ decreased rapidly. These results indicated that the presence of SO$_2$ significantly weakened the NH$_3$ adsorption, which was consistent with the result of Figure 12. After the introduction of SO$_2$ for 20 min, bands at 1373 cm$^{-1}$, 1280 cm$^{-1}$, 1095 cm$^{-1}$ and 1043 cm$^{-1}$ were detected. The band at 1373 cm$^{-1}$ could be attributed to the asymmetric vibration of O = S = O covalent groups and bands at 1280 cm$^{-1}$, 1095 cm$^{-1}$ and 1043 cm$^{-1}$ were assigned to SO$_4^{2-}$ three-fold degeneracy asymmetric stretching vibration v3. In our previous study [12], the SCR reaction over V-0.2Ce/Ti–Zr obeyed the E-R mechanism. Hence, as an important reaction substance, the weakening of NH$_3$ adsorption would greatly inhibit the SCR reaction.
3.4. Possible SO\textsubscript{2} Reaction Mechanism Over The Catalyst

The adsorption ability of SO\textsubscript{2} had something with its concentration. There was no adsorption when SO\textsubscript{2} concentration was low, which explained the stable activity of catalysts at low SO\textsubscript{2} concentration. With the increase of the SO\textsubscript{2} concentration, SO\textsubscript{2} and SO\textsubscript{4}\textsuperscript{2–} adsorption appeared. SO\textsubscript{2} was adsorbed on the surface in the form of SO\textsubscript{3}\textsuperscript{2–}. The consumption of surface OH species meant that SO\textsubscript{2} was able to react with surface hydroxyl groups to form adsorbed H\textsubscript{2}O. It was speculated that in the presence of O\textsubscript{2}, SO\textsubscript{2} would react with NH\textsubscript{3} to form (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, which could deposit on the surface of the catalyst and reduce the catalyst activity. The sulfate products could combine with Ce to form more stable Ce(SO\textsubscript{4})\textsubscript{2}. The reaction might be proposed as follows:

\begin{align*}
\text{SO}_2(g) + O^{2–}(a) &\rightarrow \text{SO}_3^{2–}(a), \quad (1) \\
\text{SO}_2(g) + 2\text{OH}^–(a) &\rightarrow \text{SO}_3^{2–}(a) + \text{H}_2\text{O}, \quad (2) \\
\text{O}_2(g) &\rightarrow 2\text{O}[a], \quad (3) \\
\text{SO}_3^{2–}(a) + [\text{O}](a) &\rightarrow \text{SO}_4^{2–}(a) \quad (4) \\
\text{SO}_4^{2–}(a) + 2\text{NH}_4^+(a) &\rightarrow (\text{NH}_4)_2\text{SO}_4 \quad (5) \\
\text{Ce}^{4+} + \text{SO}_4^{2–} &\rightarrow \text{Ce}({\text{SO}_4})_2 \quad (6)
\end{align*}

According to the in-situ DRIFTS results and other study [19], SO\textsubscript{2}(SO\textsubscript{3}\textsuperscript{2–}) could react with V\textsuperscript{5+}-OH to form VOSO\textsubscript{4} intermediate.

\[ \text{SO}_3^{2–}(a) + \text{V}^{5+}\text{-OH}(a) \rightarrow \text{VOSO}_4 \quad (7) \]

With the time passing, absorbed SO\textsubscript{2} (SO\textsubscript{3}\textsuperscript{2–}) contacted with the active component Ce and caused the transformation from Ce\textsuperscript{4+} to Ce\textsuperscript{3+}, increasing the oxygen vacancy and enhancing the NH\textsubscript{3} adsorption ability, which can explain the recovery of activity. The presence of O\textsubscript{2} promoted the redox of SO\textsubscript{2} and formation of sulfate Ce\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.

\[ 3\text{SO}_2 + 2\text{CeO}_2 + \text{O}_2 \rightarrow \text{Ce}_2(\text{SO}_4)_3 \quad (8) \]

4. Conclusions

Catalyst activity test results showed that low concentration SO\textsubscript{2} (<0.02%) had little influence on catalyst activity. With increasing SO\textsubscript{2} concentration, NO\textsubscript{x} conversion of the catalyst gradually decreased but could restore to the original level when stopping feeding SO\textsubscript{2}. A reversible deactivation would occur in the presence of H\textsubscript{2}O. However, in the presence of SO\textsubscript{2} and H\textsubscript{2}O, the catalyst was irreversibly deactivated, which was worse than that of adding SO\textsubscript{2} or H\textsubscript{2}O alone.

The characterization results showed that the BET specific surface area of the catalysts poisoned by SO\textsubscript{2} were reduced, and the redox capacity were significantly weakened. The sulfuration of the active component Ce and the deposition of ammonium sulfate might be the causes of the deactivation. XPS analysis showed that the presence of SO\textsubscript{2} promoted the generation of Ce\textsuperscript{3+}, which probably promoted the SCR reaction.

In situ DRIFTS analysis indicated that the adsorption capacity of SO\textsubscript{2} was enhanced in the presence of O\textsubscript{2}. The presence of SO\textsubscript{2} would inhibit the adsorption of NH\textsubscript{3}. At the same time, the NO adsorption ability of the catalyst was enhanced to some extent by SO\textsubscript{2}. Moreover, the NH\textsubscript{3} adsorption ability of the catalyst with pre-adsorption of SO\textsubscript{2} + O\textsubscript{2} was markedly enhanced, indicating that when SO\textsubscript{2} + O\textsubscript{2} existed, more Ce\textsuperscript{3+} and oxygen vacancy were produced. These conclusions might contribute to a better understanding of the SO\textsubscript{2} poisoning mechanism over the V\textsubscript{2}O\textsubscript{5–CeO\textsubscript{2}/TiO\textsubscript{2–ZrO\textsubscript{2}} catalyst.

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