A Comparative Study of the NH$_3$-SCR Reactions over an Original and Sb-Modified V$_2$O$_5$–WO$_3$/TiO$_2$ Catalyst at Low Temperatures

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Abstract: Considering the practical requirements for continuous operation under part load condition, the commercial honeycomb selective catalytic reduction (SCR) catalyst was modified with Sb addition. Experiments were performed to investigate the effect of modification on long-time SCR performance under part load condition. Characterizations for the original and modified catalysts were also conducted to analyze the changes of the catalysts. The results indicated that the activity of modified catalyst was obviously enhanced in the temperature range of 275–325 °C and it achieved about 64.5% removal efficiency during the 30 h stability test at 275 °C. The characterization results indicated that the ammonium sulfate was chemically adsorbed on the catalyst surface at low temperatures, which led to the decrease of the specific surface area, pore volume, and V$^{4+}$/V$^{5+}$ ratio of the catalysts. These are the reasons for the decrease of the catalyst activity at low temperatures, while the deposition amount of ammonium sulfate was relatively small over the modified catalyst. In addition, the decomposition temperature of the ammonium sulfate was reduced in the modified catalyst compared with the original one. NH$_4^+$ ions decomposed at 275 °C by reacting with the NO$_x$ in the flue gas, and the dynamic equilibrium of this reaction was achieved on the modified catalyst after a short period of time. Therefore the modified catalyst can be continuously and stably operated at this temperature, and the part load operation of the SCR system in the coal-fired power plant can be realized.

Keywords: SCR; Sb modification; part load; V$_2$O$_5$; ammonium sulfate

1. Introduction

Among the techniques for removing nitrogen oxide, selective catalytic reduction (SCR) that uses NH$_3$ as a reducing agent has become the top choice internationally for the efficient control of NO$_x$ emissions. The popularity of this method is due to its high reduction efficiency and the maturity of the technology involved. The catalyst used in SCR is essential to this technique. Currently, the main commercial catalyst used for SCR is the V$_2$O$_5$–WO$_3$ (MoO$_3$)/TiO$_2$ catalyst, which is available in honeycomb, plate, and corrugated forms. The V$_2$O$_5$–WO$_3$ (MoO$_3$)/TiO$_2$ catalyst has been widely used in flue denitrification in power plants, with an active temperature window of 300 °C–400 °C, namely, a medium-temperature SCR catalyst [1,2].

In the actual operations of power plants, the reduced utilization rate of coal-fired units has led to a substantial increase in the duration that units operate under part load conditions and low gas temperatures. The flue gas temperature produced by part load is generally lower than 300 °C; under these conditions, the denitrification performance of the catalyst decreases on decreasing the
temperature. Additionally, the SO$_2$, SO$_3$, and H$_2$O in the flue gas react with NH$_3$ to produce ammonium bisulfate (ABS), which adsorbs into the micropores of the catalyst, and blocks the micropores of the catalyst, or bonds with fly ash to form large particles that cover the surface of the catalyst [3,4]. These phenomena cause catalyst deactivation, which decreases the efficiency of the SCR system; consequently, the system fails to meet its standard, or excess ammonia slip occurs [5,6]. Therefore, a catalyst with improved low temperature performance needs to be developed to ensure continuous and stable operation under part load, thereby enabling denitrification facilities to satisfy emission requirements.

In recent years, studies on low- and medium-temperature SCR catalysts have primarily focused on catalyst systems in which V$_2$O$_5$, MnO$_2$, and CeO$_2$ are the active components [7–18]. Low-temperature performance of vanadium-based catalysts can be enhanced primarily by increasing the vanadium content. However, increasing V$_2$O$_5$ content also increases the catalyst’s ability to oxidize SO$_2$ under high temperatures, leading to increased formation of SO$_3$ and affecting downstream equipment. Moreover, ABS deposits remain on the catalyst surface, causing catalyst deactivation. Manganese and cerium-based catalysts exhibit favorable denitrification performance under low-to-medium temperature conditions. However, the active components easily react with SO$_2$ and H$_2$O in flue gas to form sulfate, leading to a rapid decline in the denitrification performance of the catalyst, which limits its potential for industrial application [19,20]. Modification of commercial catalysts to reduce the deposition temperature of ABS on catalyst surfaces offers a direction for the development of a part load SCR catalyst.

In this study, commercial catalysts were used as a basis for the preparation of a modified honeycomb SCR catalyst. Activity tests using simulated flue gas over a long period were conducted. Characterization methods such as N$_2$ physisorption, scanning electron microscope (SEM) mapping, X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and thermogravimetry were employed to analyze the experimental results, and an optimized SCR catalyst suitable for use at 275 °C–400 °C was obtained.

2. Experimental Methods

2.1. Catalyst Preparation

A commercial honeycomb catalyst manufactured by Zheneng Catalyst Technology Co., Ltd. (Haining city, Zhejiang, China) was used as a basis. The inner-wall thickness of the catalyst was 0.7 mm, and the pore diameter was 6.1 mm. The catalyst was modified using the incipient wet impregnation (IWI) method. The specific preparation method was as follows: A precursor solution containing a certain amount of Sb$_2$O$_3$ was prepared. Subsequently, the commercial honeycomb catalyst was placed in the solution, which was then kept at 60 °C for 2 h. The loaded catalyst was dried at 120 °C for 12 h, and then calcinated at 400 °C for 5 h to obtain a modified version. The commercial catalyst was labeled VWTi, and the modified one was labeled VWSbTi.

2.2. Activity Test

The honeycomb catalyst was cut into a 50 mm × 50 mm × 200 mm block and placed into a fixed bed reactor for denitrification performance evaluation. The gaseous N$_2$, O$_2$, SO$_2$, NO, and NH$_3$ were used and controlled by mass flow meters, while SO$_3$ was formed from the oxidation of SO$_2$ and O$_2$. A specific amount of water was used and fed to the vaporizer. Following heating and vaporization, it then entered the reactor. The tail gas was measured using an MGA-5 infrared flue gas analyzer (MRU Instruments Inc., Germany); specifically the gas concentrations at the inlet and outlet of the reactor were determined.

Typical flue gas conditions were as follows: 300 ppm NO, 1.05 of NH$_3$/NO ratio, 500 ppm SO$_2$, 20 ppm SO$_3$, 10% water vapor, 5% O$_2$, and N$_2$ as a carrier gas, with a total flow rate of 40.7 L/min,
achieving a gas hourly space velocity (GHSV) of 10,000 h\(^{-1}\). The equation used for calculating efficiency is as follows:

\[
X = \frac{C_{\text{in}} \text{NO} - C_{\text{out}} \text{NO}}{C_{\text{in}} \text{NO}} \times 100\% \tag{1}
\]

where \(C_{\text{in}} \text{NO}\) and \(C_{\text{out}} \text{NO}\) represent the NO concentrations at the inlet and outlet of the reactor, respectively.

### 2.3. Catalyst Characterization

The specific surface areas, pore volumes, and pore diameters of the catalysts were measured using an ASAP2020 physisorption analyzer as well as by a \(N_2\) physisorption method, in which an adsorption temperature of 77 K was employed. Before sample testing, the sample was dried under conditions of 1.5 Pa and 200 °C for 4 h. The specific surface areas of the catalysts were calculated using the Brunauer–Emmett–Teller (BET) equation, while the total pore volumes were derived from the amount of nitrogen adsorbed at \(P/P_0 = 0.95\). The morphology of the prepared samples was characterized by SEM (Quanta FEG 250) and element distribution was acquired through mapping simultaneously.

XRD analysis was performed using a polycrystalline X-ray diffractometer (D/max 2550 PC, Rigaku Inc., Tokyo, Japan) equipped with X-ray tube accelerating by 40 kV, 200 mA towards a Cu target with scan angle of 10°–90° and scanning speed of 4°·min\(^{-1}\). Raman spectra were collected employing a Renishaw inVia rig using an Ar ion laser (wavelength of 514.4 nm).

An X-ray fluorescence spectrometer (ZSX 100e, Rigaku Inc., Tokyo, Japan) was employed in the XRF analysis to determine the content of each component of the catalyst sample.

XPS analysis was performed using an X-ray photoelectron spectrometer (Escalab 220i-XL, VG Thermo Inc., Waltham, MA, USA). A 300 W Mg Kα radiation source was used under a pressure of \(3 \times 10^{-9}\) mbar, and the obtained spectra were calibrated using C 1s electron binding energy (284.8 eV).

FT-IR analysis was performed using a Fourier transform infrared spectrometer (NICOLET NEXUS 670, Thermo Fisher Scientific Inc., Waltham, MA, USA). The catalyst was mixed with KBr, ground, pressed, and placed in an infrared light path. The infrared scan range was 4000–400 cm\(^{-1}\), and the scan resolution was 4 cm\(^{-1}\).

Thermogravimetric analysis was performed using a thermogravimetric analyzer (TG-Q500, TA Instruments Inc., New Castle, DE, USA). During the experiment, 3 mg solid powder sample was weighed and placed in a crucible, and \(N_2\) was used as the carrier gas. For pretreatment to remove water and other impurities adsorbed onto the sample surface, the temperature was increased to 100 °C at a heating rate of 10 °C·min\(^{-1}\) for 30 min. Subsequently, the temperature was increased to 650 °C at a heating rate of 10 °C·min\(^{-1}\).

### 3. Results and Discussion

#### 3.1. Activity Tests

The effect of temperature on the deNO\(_x\) performance is shown in Figure 1. With the increase of temperature, the deNO\(_x\) efficiencies increased accordingly. Compared to sample VWTi, the efficiency of VWSbTi reached 79.3% at 275 °C, and 16.4% increment was obvious. However, when the temperature was raised up to 350 °C, the efficiencies of the two catalyst were 86.1% and 90.7%, respectively, and a slight increment of 4.6% was evident. The performance was inclined to unity at 400 °C. Since our previous results confirmed that the introduction of Sb slightly affected SCR selectivity below 400 °C [21], these features implied that modification improved the performance of catalyst at lower temperatures, especially in the range 275 to 325 °C.
To evaluate the long term activity, tests at 275 °C spanning 30 h were carried out and results are shown in Figure 2. Moreover, to simulate the real flue gas, SO$_2$, SO$_3$, and H$_2$O were also included. It was shown that after 3 h, deNO$_x$ efficiency for VWTi increased from 58.6% to 61.9%. This implied that in the initial stage, sulfate was formed over the catalyst surface due to the introduction of SO$_x$ in the flue gas, which increased the acidity of catalyst, promoting the activity. However, this benefit remained short term and the efficiency decreased gradually to 43.6% after 30 h. Compared to the maximum value, 18.3% decrement was evident and the calculated loss rate was 0.68%/h. The possible reason may be due to the formation of ammonium sulfate, which covered the active sites of the catalyst surface, resulting in deactivation. A different behavior was observed over the modified catalyst, namely, VWSbTi. The profile of VWSbTi in Figure 2 could be divided into two stages. In the first stage, ending at 18 h, the activity gradually decreased from 76.1% to 64.5%, with a rate of 0.64%/h similar to that of VWTi. It implied that in the first stage, part of the ammonium sulfate was formed and deposited over the catalyst surface, resulting in declined activity. With the reaction proceeding, namely, from 18 h to 30 h, the profile levelled off, maintaining around 64.5%. The unique performance of modified catalyst may be due to the equilibrium of ammonium sulfate reached over the catalyst surface, leading to stable activity.
3.2. Characterization of Catalysts

Since the modified catalyst showed considerable improvement, the physical and chemical properties of the catalysts were investigated to correlate performance with properties by means of several characterization methods.

3.2.1. XRF Results

The results of XRF are shown in Table 1. Note that after modification, 2.1 wt% Sb$_2$O$_3$ was introduced to the original catalyst, resulting in slight decrease of content of V$_2$O$_5$, WO$_3$, and TiO$_2$. It indicated that the preparation method exerted little effect on the main components of the catalyst. In addition, some sulfate species were also found in both of the fresh samples, possibly derived from the impurity in the precursors. After long term reactions, the obvious increase of sulfate species was evident with little change regarding other components. Specifically, SO$_3$ content of VWTi after reaction was 2.00%, showing a 1.793% increase while that of VWSbTi after reaction was 1.15% with a 0.972% increment. It implied that ammonium sulfate was deposited over both catalysts while less deposition was obvious over VWSbTi, consistent with previous activity tests, which showed less deactivation over VWSbTi.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V$_2$O$_5$, wt%</th>
<th>WO$_3$, wt%</th>
<th>Sb$_2$O$_3$, wt%</th>
<th>TiO$_2$, wt%</th>
<th>SO$_3$, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VWTi</td>
<td>0.906</td>
<td>2.01</td>
<td>-</td>
<td>88.1</td>
<td>0.207</td>
</tr>
<tr>
<td>VWSbTi</td>
<td>0.838</td>
<td>1.96</td>
<td>2.10</td>
<td>85.8</td>
<td>0.178</td>
</tr>
<tr>
<td>VWTi-r</td>
<td>0.912</td>
<td>1.97</td>
<td>-</td>
<td>85.8</td>
<td>2.00</td>
</tr>
<tr>
<td>VWSbTi-r</td>
<td>0.813</td>
<td>1.94</td>
<td>2.04</td>
<td>85.1</td>
<td>1.15</td>
</tr>
</tbody>
</table>

-r represents the sample after SCR reaction.

3.2.2. N$_2$ Adsorption and SEM Mapping Results

Specific areas, pore volumes, and mean pore diameters for catalysts before and after reaction are listed in Table 2. The results showed that after modification, the specific area and pore volume decreased to some extent, implying that loaded materials were deposited in the pore structure. After reaction, decline of both specific areas and pore volumes was observed for both catalysts, namely, VWTi and VWSbTi, due to the deposition of ammonium sulfate. Moreover, deposition of ammonium sulfate showed less effect on pore structure for sample VWSbTi, compared to that of VWTi. It is again in good agreement with the activity performances, which showed less severe deactivation over VWSbTi. To further understand the effect of Sb doping, SEM images and the elemental distribution of V, W, and Sb of the VWSbTi sample were obtained and are shown in Figure 3. Figure 3 clearly demonstrates the uniform distribution of V, W, and Sb, implying the IWI method is suitable for catalyst modification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Areas, $m^2$/g</th>
<th>Pore Volume, $cm^3$/g</th>
<th>Mean Pore Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>VWTi</td>
<td>55.7</td>
<td>0.285</td>
<td>16.9</td>
</tr>
<tr>
<td>VWSbTi</td>
<td>50.5</td>
<td>0.273</td>
<td>17.6</td>
</tr>
<tr>
<td>VWTi-r</td>
<td>42.6</td>
<td>0.263</td>
<td>18.3</td>
</tr>
<tr>
<td>VWSbTi-r</td>
<td>45.1</td>
<td>0.272</td>
<td>17.4</td>
</tr>
</tbody>
</table>

-r represents the sample after selective catalytic reduction (SCR) reaction.
3.2.3. XRD and Raman Results

To illustrate the change of crystal, XRD was employed to investigate the catalyst before and after reaction, as shown in Figure 4a. All the samples exhibited typical anatase of TiO$_2$ before and after reaction, and no other phase was detected. It is suggested that contents of other components, such as V$_2$O$_5$, WO$_3$ and ammonium sulfate are too low to form large crystal particles, reflected by XRD. However, this trend could not be ruled out. Besides XRD diffraction patterns, Raman spectra were also collected over different samples, illustrated in Figure 4b. Five obvious peaks centering at 136, 188, 387, 506, and 630 cm$^{-1}$ were observed, ascribed to Ti–O bonds [22]. Given that the sulfur species were introduced, no shifts for the peaks were observed, implying Ti–O bonds remain unchanged during the reactions. In contrast, after Sb doping the intensity of the peaks prominently increased, indicating crystal growth of TiO$_2$ [23]. However, this trend could not be clearly detected by XRD patterns in Figure 4a due to the detection limit.

![Figure 3. SEM mapping photograph of V, W, Sb within a local part of the VWSbTi sample.](image)

![Figure 4. (a) XRD diffraction patterns and (b) Raman spectra for different samples.](image)
3.2.4. XPS Results

XPS spectra were used to characterize the electronic environment change around the atom, as shown in Figure 5. As for Ti 2p spectra, binding energies located at 458.6 eV and 464.3 eV belong to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ of Ti$^{4+}$, respectively [21]. As illustrated in Figure 5a, Ti was in a +4 oxidation state both before and after the reaction, and the catalyst modification exhibited little effect on the electron spectrum of Ti. After the reaction, however, the VWTi catalyst shifted to a high binding energy, with an increase of approximately 0.3 eV, which indicated that the electron cloud density around the Ti atoms decreased after ABS deposition [24]. The Ti binding energy of the VWSbTi catalyst exhibited no major differences after the reaction, possibly because of the relatively small deposition of ABS.

![Figure 5a](image1.png)

![Figure 5b](image2.png)

![Figure 5c](image3.png)

*Figure 5. Cont.*
For the V 2p spectra, V with a binding energy of 515.4–516.0 eV was attributed to V$^{4+}$, and V at 516.6–517 eV was attributed to V$^{5+}$ [25]. The ratio of V$^{4+}$/V$^{5+}$ was a crucial factor affecting the denitrification activity of the catalyst. At a relatively low oxidation state, the vanadium species was more conducive to electron transfer. Within a certain range and under the same conditions, a larger V$^{4+}$/V$^{5+}$ ratio led to higher denitrification activity of the catalyst [26]. As depicted in Figure 5b, the content of V$^{4+}$ decreased significantly after the reactions of the two catalysts. According to the calculations, the respective V$^{4+}$/V$^{5+}$ ratios of the VWTi and VWSbTi catalysts before the reaction were 0.598 and 0.588, and those after the reaction were 0.384 and 0.503. Thus, the V$^{4+}$/V$^{5+}$ ratio of the VWTi catalyst decreased to a greater extent after the reaction. Additionally, the VWSbTi catalyst shifted to a higher binding energy, with an increase of approximately 0.3 eV, than did the VWTi catalyst. This indicated that although catalyst modification affected the electron environment surrounding the V atoms, it did not significantly change the V$^{4+}$/V$^{5+}$ ratios in the catalysts. Therefore, the catalysts did not exhibit substantial changes in high temperature activity. After the reaction had been conducted for a long duration under low temperatures, the V$^{4+}$/V$^{5+}$ ratio decreased considerably, leading to a decrease in catalyst activity. Additionally, for the VWTi catalyst, the V$^{4+}$/V$^{5+}$ ratio decreased to a greater degree following the reaction, and the catalyst activity also decreased. This result is consistent with those of the activity tests shown in the previous section.

Regarding the O 1s spectra, oxygen with a binding energy of 529.9–530.15 eV was attributed to lattice oxygen O$^{2−}$(O$_{β}$), and oxygen at 531.5–531.7 eV was attributed to chemisorbed oxygen O$_{α}$, including oxygen from hydroxide and vacancy [27]. The proportions of chemisorbed oxygen (O$_{α}$/(O$_{α}$ + O$_{β}$)) in the catalyst samples VWTi and VWSbTi before reaction and after reaction were 11.39%, 13.88%, 24.34%, and 21.19%, respectively. After catalyst modification, the proportions of chemisorbed oxygen increased. Chemisorbed oxygen on the catalyst surface can promote SCR reaction [28], and this effect may have contributed to the increased activity of the modified catalyst. However, after 30 h reaction, the amount of chemisorbed oxygen on the catalyst surfaces increased substantially. This
may be due to the ammonium sulfate deposition. The sulfate species may have bonded with H by a bridging bidentate ligand, thereby forming a Brønsted acid site [29]. Thus, the number of Brønsted acid sites may have increased and formed more hydroxyl groups, resulting in an increase in the proportion of chemisorbed oxygen on the catalyst surface. However, in this case the increase in the amount of chemisorbed oxygen did not cause an increase in catalyst activity.

For the N 1s spectra, N with a binding energy of 401.1–401.6 eV was attributed to NH$_4^+$ [19] and N with a binding energy of 398.4 eV was attributed to the N in the precursor from catalyst preparation. During catalyst modification, after the catalyst had been dried and calcined, the N contained in the precursor entered the catalyst. As denoted in the Figure 5d, after 30 h reaction, compared to VWTi, the NH$_4^+$ in the VWSbTi catalyst shifted to a lower binding energy, which indicated that the electron cloud density surrounding the N atoms increased. This result may have been related to the effects of doping with nitrogen-containing species or metal oxide.

The peak of S 2p is illustrated in Figure 5e. The S peaks in the four catalysts could be divided into two components, namely, S 2p$_{1/2}$ (168.2–168.5 eV) and S 2p$_{3/2}$ (169.2–169.5 eV). These results indicated that the S in the catalysts was at a +6 oxidation state and existed in the form of SO$_4^{2-}$ [30,31], and that ammonium sulfate was present on the catalyst surface after the reaction. Compared with the VWTi catalyst after reaction, the S peak in VWSbTi after reaction decreased in binding energy by 0.3 eV, indicating that the electron cloud of S on the VWSbTi catalyst after reaction was relatively dense. During the decomposition of ABS, the decomposition product of SO$_4^{2-}$ was SO$_2$, and the oxidation state of S decreased. Therefore, based on the S 2p results an inference was established that the S in the VWSbTi catalyst was relatively easy to reduce.

3.2.5. FT-IR Results

The infrared spectra of the catalyst before and after the reaction are illustrated in Figure 6. These spectra results were used to analyze changes in the surface functional groups of the catalysis before and after the reaction. The peaks at 972, 1042, 1124, 1136, and 1225 cm$^{-1}$ were attributed to vibration of SO$_4^{2-}$ while 1400 cm$^{-1}$ was attributed to the asymmetric bending vibration of NH$_4^+$, bonded with the Brønsted acid site. The peak at 1630 cm$^{-1}$ was attributed to the vibration peak of H$_2$O adsorbed on the catalyst surface [32,33]. Before the catalyst reaction, peaks occurred at 1042 cm$^{-1}$ and 1124 cm$^{-1}$, indicating the presence of sulfate. After the reaction, the peak at 1124 cm$^{-1}$ shifted to 1136 cm$^{-1}$, and a new peak appeared at 1225 cm$^{-1}$. These two peaks represented symmetric and asymmetric stretching vibrations of S=O, whereas the peak at 972 cm$^{-1}$ was attributed to the symmetric stretching vibration of S−O [34]. Thus, after the ammonium sulfate was deposited on the catalyst surface, it generated a mutual effect with the catalyst. Specifically, the ammonium sulfate was chemisorbed on the catalyst surface, forming a bidentate SO$_4^{2-}$ and interacting with TiO$_2$, thereby creating the mutual effect [35].

![Figure 6. FT-IR spectra of various samples.](image)
3.2.6. Thermogravimetric Results

The cause of the increased stability in catalyst activity observed at low temperatures after catalyst modification was examined. The IWI method was employed to load 10% ABS separately on VWTi and VWSbTi for thermogravimetric analysis. The two samples were labeled ABS-VWTi and ABS-VWSbTi. A thermogravimetric analysis of a pure ABS sample was also performed for comparison, and the thermogravimetric (TG) and differential thermogravimetry (DTG) curves are presented in Figure 7. The pure ABS exhibited only one peak near 370 °C in the DTG curve; at this temperature, ABS completely decomposed. When ABS was loaded onto the VWTi and VWSbTi catalysts, different decomposition behaviors were observed. For ABS-VWTi, two peaks (375 °C and 470 °C) appeared while for ABS-VWSbTi, in addition to the two peaks at 361 °C and 433 °C, a small peak was evident at 265 °C. The three peaks at 265 °C, 361 °C, and 375 °C were all attributed to NH$_4^+$ consumption, whereas the peaks at 433 °C and 470 °C were primarily attributed to the decomposition of SO$_4^{2-}$ [35,36]. The decomposition temperature for ABS-VWSbTi was lower than that for ABS-VWT, indicating that catalyst modification resulted in a lower ABS decomposition temperature. By combining XPS, FT-IR, and thermogravimetric results, it was inferred that when the catalyst was operating at 275 °C, ammonium sulfate formed and chemisorbed onto the surface of the catalyst, resulting in the formation of NH$_4^+$ and SO$_4^{2-}$. The decomposition temperature of NH$_4^+$ over modified catalyst was lower than that of original one. At this temperature, the decomposed NH$_4^+$ reacted with the NO$_x$ in the flue gas. The formed SO$_4^{2-}$ exhibited a mutual effect with TiO$_2$, and this mutual effect was reversible and easy to regenerate. Only a portion of TiO$_2$ was sulfated [33]. Therefore, after a certain period, dynamic equilibrium was achieved on the surface of the modified catalyst, compared to the continuous decline trend observed over the original one.

![Figure 7](https://example.com/figure7.jpg)

**Figure 7.** Thermogravimetric curves of different samples. (a) TG and DTG curves of pure ammonium bisulfate (ABS); (b) TG and DTG curves of ABS-VWTi and ABS-VWSbTi.
4. Conclusions

(1) Modification of the commercial SCR catalyst significantly increased the denitrification performance of the catalyst in the temperature range of 275–325 °C. After 30 h of operation at 275 °C, the efficiency stabilized at 64.5%, whereas that of the original one continued to decline.

(2) Catalyst characterization results revealed that after 30 h of continuous operation at 275 °C, both of the catalysts exhibited ammonium sulfate deposition. The deposition led to a decrease in the specific surface area, pore volume, and $V^{4+} / V^{5+}$ ratio, and these changes caused a decline in catalyst activity at low temperatures. However, the ammonium sulfate deposition over the modified catalyst was relatively low.

(3) The XPS, FT-IR, and thermogravimetric results revealed that the deposited ammonium sulfate chemisorbed on the catalyst surfaces, resulting in formation of $\text{NH}_4^+$ and $\text{SO}_4^{2-}$. However, catalyst modification caused a decrease in the deposition temperature of ammonium sulfate on the catalyst. At 275 °C, the decomposed $\text{NH}_4^+$ reacted with the $\text{NO}_x$ in the flue gas, whereas the generated $\text{SO}_4^{2-}$ interacted with TiO$_2$. The interaction between TiO$_2$ and $\text{SO}_4^{2-}$ was reversible and easy to reproduce; the surface of the TiO$_2$ only becoming partially sulfated. After a certain period, dynamic equilibrium was reached on the surface of the modified catalyst, increasing the stability of the catalyst’s operation at this temperature. This indicated that after modification, the catalyst could operate continuously at low temperatures; thus, the catalyst can be used for part load operation in coal power plants.

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