

Effect of V₂O₅ Supported on the Sulfated TiO₂ for Low-temperature SCR of NO by NH₃

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Abstract

V₂O₅-WO₃/TiO₂-SO₄²⁻ catalysts were prepared by wet impregnation method with sulfated nano-TiO₂. Different acid amounts, activities, sulfur tolerance and regeneration of the catalysts were tested. It was found that the low-temperature catalytic activity of V₂O₅-WO₃/TiO₂-SO₄²⁻ was improved after modified with 0.4M H₂SO₄. BET and XRD results showed that the specific surface area of catalysts decreased after sulfating without crystal form changing. The catalytic activity of V₂O₅-WO₃/TiO₂-SO₄²⁻ catalyst was better than the original, which decreased from 95% to 90% in 50h under the condition of 300ppm SO₂ at temperature of 180°C. FT-IR and TG results showed that the deactivation by SO₂ was due to the ammonium sulfate forming during the SCR reaction. The activity of poisoned catalysts could be recovered to the fresh level after calcined at 490°C.

Keywords: Acidification; SCR; Sulfur Tolerance; Regeneration

1 INTRODUCTION

Nitrogen oxide (NO_x) emissions are the main sources of air pollution which have harmful effects on the environment and human health (Mauzerall D L, et al., 2005). Selective catalytic reduction (SCR) of nitrogen oxides with ammonia is one of the widely used processes for cleaning the flue gas from stationary sources and diesel engines (Teng H, 1999). The general SCR reaction is: $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$.

SCR catalysts are the most critical factor in the selective catalytic reduction process. A large number of SCR catalysts have been studied in the literature that V₂O₅/TiO₂ catalyst has been widely applied in NO_x removal. Such commercial catalyst has excellent activity in the SCR reaction within a narrow high temperature range (Busca G, et al., 1998). However, it is necessary to locate the SCR unit upstream of the desulfurizer and electrostatic precipitator in order to avoid reheating of the flue gas as well as deposition of dust on the catalyst (H. Bosch, 1988). For this reason, it is urgent to develop a superior SCR catalyst that exhibits high activity at wide low temperature between 120-400°C to ensure the catalyst deactivation could be avoided. Previous studies have shown that the SCR activity could be improved by the catalysts doping with SO₄²⁻ ion as TiO₂ promoter. The support TiO₂ impregnated with H₂SO₄ has high activity in high temperature reactions between 400°C and 600°C (Chen J P, 1993; Jung S M, 2000). Alemany L J et al (Alemany L J, 1996) found that the specific surface area and total pore volume of TiO₂ was increased after doping the SO₄²⁻. Moreover, It has been reported that Brønsted acid which provided by SO₄²⁻ on TiO₂ could maintained a superior SCR activity at low temperature (Sun Q, 2008; Ciambelli P, 1996). It has been also proposed that SO₄²⁻ produces a strong acidic site which could lead to the high reactivity in the SCR reaction (Y. Tsutomu, 1990).

According to many reports in the literature, it has been shown that SO₄²⁻ could increase the acidity and reactivity of SCR catalysts. However, until now, no studies about sulfating V₂O₅-WO₃/TiO₂ directly have been proposed. In this article, as a support material, TiO₂ anatase was modified with SO₄²⁻ directly. V₂O₅-WO₃/TiO₂-SO₄²⁻ catalysts were carried out by two-step wet impregnation method. Different acid amounts, activity, sulfur tolerance and regeneration of the catalysts were tested. We further investigated the mechanism of SO₂ deactivation process of V₂O₅-WO₃/TiO₂-SO₄²⁻ catalysts using BET, FT-IR and TG.

2 EXPERIMENT

2.1 Catalyst Preparation

The V_2O_5 - WO_3 / TiO_2 - SO_4^{2-} catalysts were prepared by two-step wet impregnation method. To obtain the sulfated catalyst, required amounts of TiO_2 were added to a 200mL beaker within 50mL H_2SO_4 solution (0.0-1.0M). The support solution was stirred continuously for 2h. The resulting solids were oven dried at 105°C for 4h, then calcined at 490°C for 3h. The sulfated supports were ground and sieved to 100 mesh size.

V_2O_5 - WO_3 / TiO_2 - SO_4^{2-} catalysts employed in the present study containing V_2O_5 and WO_3 were prepared by aqueous solution of NH_4VO_3 and $(NH_4)_{10}W_{12}O_{41}$ diluted in oxalic acid in a desired proportion. The calculated amount of sulfated TiO_2 support was impregnated in this solution by stirring for 2h. The resulting materials were oven dried at 105°C for 4h, then calcined at 490°C for 3h. The catalysts were ground and sieved (20-40 mesh) to obtain homogeneous powder.

2.2 Catalyst Characterization

The surface areas of the catalyst powders were measured by physical nitrogen adsorption at -196°C using Micromeritics Gemini V. The catalysts (0.1 – 0.2 g) were degassed at 110°C for 1 h.

The X-ray diffraction (XRD) measurements were performed with Cu Ka ($k = 0.15406$ nm) radiation. The catalysts were run at 2 θ , ranging from 10° to 80° with a step size of 0.020° and a time step of 1.0 s using Bruker D8.

FT-IR spectra were recorded using a Bruker VECTOR22 spectrometer with a wave number range from 400 to 4000 cm^{-1} and a spectral resolution of 4 cm^{-1} . The samples were pressed with KBr.

Thermo gravimetric analysis (TG) for the different series of catalyst was carried out in a TG/DTA6300 with sensitivity of 0.1 μg . The samples were tested under air atmosphere from 25 to 1000°C with heating rate of 10°C/min⁻¹.

2.3 Catalytic Activity Test

The SCR activity of the catalysts for NO removal with NH_3 was carried out in a fixed-bed flow reactor (i.d. 6 mm). A temperature controller and thermo couple which used to control the temperature of the reactor were inserted directly into the catalyst bed. The reactant gas composition was as follows: 700ppm NO, 700ppm NH_3 , 300ppm SO_2 , 5vol% O_2 and N_2 as balance. The gas hourly space velocity (GHSV) was 27000h⁻¹. The feed gases were mixed before entering the reactor. The reactants and products were analysed on line using a Nitrogen Oxides Analyser, 42i-HL (Thermo Electron Corporation).

3 RESULTS AND DISCUSSION

3.1 Acid Amounts on V_2O_5 - WO_3 / TiO_2 - SO_4^{2-} Catalysts

The catalysts modified with different acid amounts were prepared to compare the activities. The reaction conditions were as follows: 700ppm NO, 700ppm NH_3 , 5% O_2 , N_2 balance, GHSV of 27000h⁻¹. According to the results from Fig.1, the activity of V_2O_5 - WO_3 / TiO_2 catalyst was obtained 30.7%, 60.5% and 90% at low temperature of 140,160 and 180°C. However, NOx removal activity of catalyst supported on sulfated TiO_2 (0.4M H_2SO_4) has been enhanced even up to 41%, 70% and 95% at low temperature of 140,160 and 180°C. It also indicated that SO_4^{2-} doping were favorable to improve the low-temperature activities of V_2O_5 - WO_3 / TiO_2 - SO_4^{2-} catalysts. However, further increase of the amount of acid to 0.5mol/L lowered the activity of the catalysts. It may be due to the presence of excess sulfate species which cover the active sites on the catalyst surface.

Therefore, it could be concluded that sulfuric acid doping had positive effect on the low-temperature activity of the catalysts (Choo S T, 2000). It was clearly observed that sulfuric species played a certain role for the Brønsted acid sites on the surface of catalysts. As for SCR reaction process, NH_3 adsorption was enhanced by the increase of the amounts and strength of the sulfate acid sites on the catalyst surface. Moreover, the effect of catalyst surface acidity was favorable for NO removal activity.

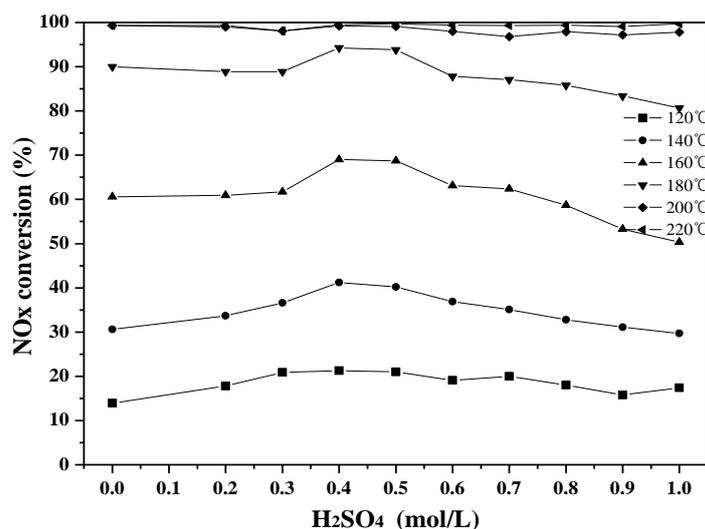


FIG. 1 NO CONVERSION OVER $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ CATALYSTS

3.2 SO_2 Tolerance and Regeneration of $V_2O_5-WO_3/TiO_2 (-SO_4^{2-})$ Catalysts

The effect of 300ppm SO_2 on SCR activity of $V_2O_5-WO_3/TiO_2$ and $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ at temperature of 180°C is illustrated in Fig.2. It could be seen that the steady NO_x conversion of $V_2O_5-WO_3/TiO_2$ and $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ were obtained 90% and 95% under the condition without SO_2 , respectively. However, in the presence of SO_2 , the catalytic activity of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ was improved slightly to 97.7%. The promotion behavior of catalyst activity may be due to the increase of the sulfuric acid sites that enhanced the NH_3 adsorption (Motonobu Kobayashi, 2006). It could be observed that the NO_x removal activity of the $V_2O_5-WO_3/TiO_2$ decreased rapidly than that of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$. In the case of 300ppm SO_2 , approximately 76% and 90% of NO conversion by $V_2O_5-WO_3/TiO_2$ and $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ remained after 50h. It was generally considered that SO_2 deactivation mechanism of SCR catalysts was mainly due to two aspects (Giakoumelou I, 2006). (1) Metal sulfate formed by SO_2 and metal oxide (active phase or support) lead to catalyst chemical deactivation. (2) Deposition on catalyst surface of ammonium sulfate/bisulfate lead to physical deactivation caused by SO_2 and NH_3 at low temperature.

To investigate the deactivation mechanism of SO_2 on the catalyst activity, the used catalyst was then regenerated by calcined at 490°C for 3h with a continuous flow of N_2 . As shown in Fig.3, the NO conversion of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ could be approximately recovered to the original levels during the temperature of 140-200°C after thermo regeneration.

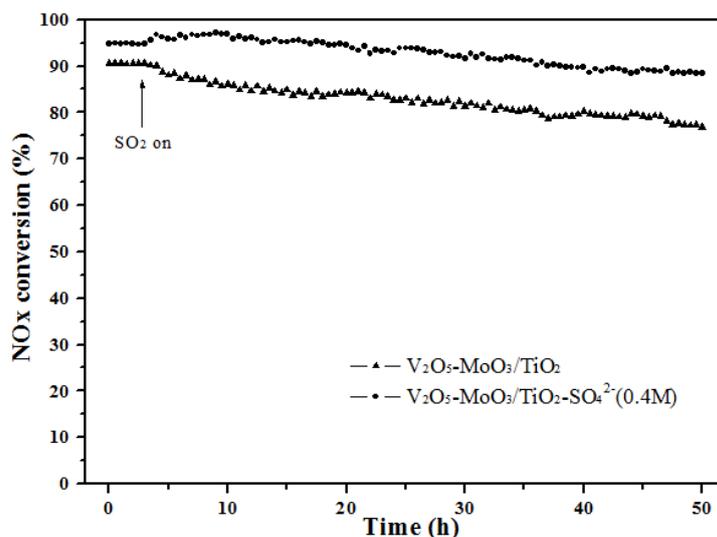


FIG. 2 EFFECT OF SO_2 ON NO CONVERSION OVER $V_2O_5-WO_3/TiO_2(-SO_4^{2-})$ CATALYSTS

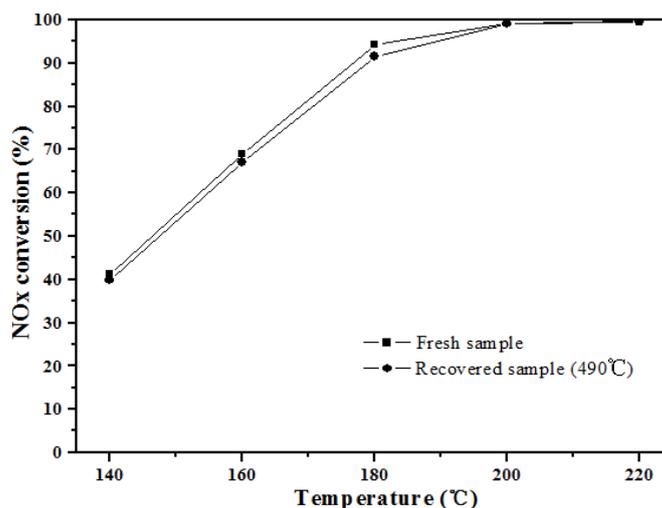


FIG. 3 ACTIVITY TEST ON RECOVERED $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ CATALYSTS

3.3 BET Surface Area and X-ray Diffraction Measurements

BET surface areas of each catalyst are summarized in Table 1. For $V_2O_5-WO_3/TiO_2$ catalyst, the specific surface area was observed to be $85 \text{ m}^2/\text{g}$. After modified with $0.2\text{M H}_2\text{SO}_4$, the specific surface area of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ catalysts decreased rapidly to $66 \text{ m}^2/\text{g}$. With the increasing concentration of sulfuric acid, the specific surface area of catalysts decreased slightly. It may be caused by nano agglomerated particles on TiO_2 that plugged part of the active sites on catalyst surface. However, as the mass fraction of SO_4^{2-} increased, the SCR activity of catalysts did not enhance further with the addition of SO_4^{2-} . $V_2O_5-WO_3/TiO_2$ modified with $0.4\text{mol/L H}_2\text{SO}_4$ amongst all the catalysts showed the best SCR activity.

TABLE 1 BET SURFACE AREA OF CATALYSTS

Mum.	Sample	BET ($\text{m}^2 \text{g}^{-1}$)
1	$V_2O_5-WO_3/TiO_2$	85
2	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.2M)	66
3	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.3M)	65
4	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.4M)	61
5	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.5M)	61
6	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.6M)	62
7	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.7M)	58
8	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.8M)	55
9	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.9M)	51
10	$V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (1.0M)	48

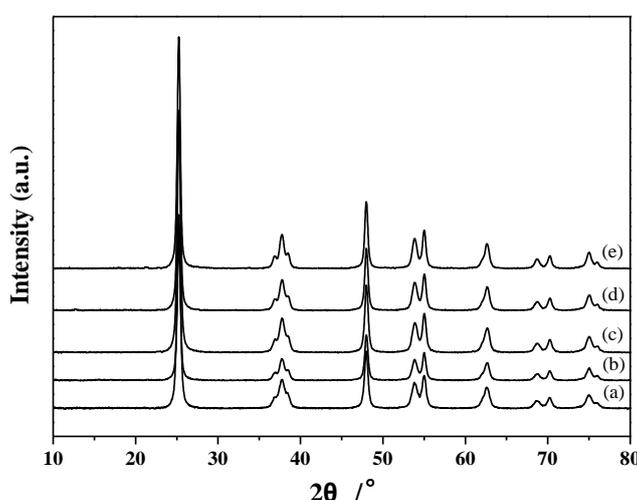


FIG. 4 X-RAY DIFFRACTION PATTERNS OF THE $V_2O_5-WO_3/TiO_2$ (a) $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.2M)(b), $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.4M)(c), $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (0.7M)(d), $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ (1.0M)(e) CATALYST

The XRD patterns of $V_2O_5-WO_3/TiO_2$ with SO_4^{2-} loadings are shown in Fig.4. For all the catalyst samples, only anatase TiO_2 oxide was detected with the increasing amounts of the sulfuric acid. It was indicated that sulfuric catalysts remained its amorphous structure with no other distinctively obvious diffraction peaks, which suggested that V_2O_5 was highly dispersed on the catalyst surface.

3.4 BET Surface Area and Pore Structure Measurements of Poisoned Catalysts

BET surface area and pore structure measurements of poisoned catalysts are listed in Table 2. The surface area of the catalyst poisoned by SO_2 was confirmed to be lowered than that of the fresh catalyst. For poisoned catalyst, the specific surface area, pore volume and average pore diameter were decreased to $57 \text{ m}^2/\text{g}$, $0.23 \text{ cm}^3/\text{g}$ and 13.7 nm , respectively. It appeared that poisoning substances generated by SO_2 would cover the active sites on the catalyst surface, which reduced the physical properties and SCR activity of the catalyst. However, after calcined at 250°C and 490°C , the specific surface area and average pore diameter increased to $63 \text{ m}^2/\text{g}$, 14.7 nm and 14.8 nm , respectively. It was clearly indicated that poisoning substances could be decomposed at the temperature of 250°C and 490°C , which improved all the physical properties to the original levels.

TABLE 2 BET SURFACE AREA AND PORE STRUCTURE OF POISONED CATALYSTS

Mum.	Sample	BET (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
1	$V_2O_5-WO_3/TiO_2-SO_4^{2-}(0.4M)$	61	0.25	14.8
2	$V_2O_5-WO_3/TiO_2-SO_4^{2-}(0.4M)$ -Poisoned	57	0.23	13.7
3	$V_2O_5-WO_3/TiO_2-SO_4^{2-}(0.4M)$ -Poisoned- 250°C	63	0.26	14.7
4	$V_2O_5-WO_3/TiO_2-SO_4^{2-}(0.4M)$ -Poisoned- 490°C	63	0.27	14.8

3.5 FT-IR and TG Analyses of Poisoned Catalysts

To identify the deactivation mechanism of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ catalysts poisoned by SO_2 for the SCR of NO with NH_3 , FT-IR spectra of fresh and spent catalysts are shown in Fig.5. All the catalysts exhibited vibration absorptions at wave numbers of 1635 cm^{-1} , which could be attributed to the absorbed water in the catalysts and KBr (Shen, 2009). Compare to the fresh catalyst, a new band at 1398 cm^{-1} was appeared for poisoned catalyst, which could be assigned to NH_4^+ species chemisorbed on the Brønsted acid sites (Sherrie Elzey, et al., 2008; Zhu, et al., 2001). Simultaneously, two new bands at 1137 cm^{-1} and 1046 cm^{-1} which were classified to the characteristic frequencies of SO_4^{2-} ion appeared (Xie, 2003; Daniela Pietrogiamomi, et al., 2002). Therefore, the results above demonstrated that ammonium sulfate species would be formed on the catalysts during the SCR reaction in the presence of SO_2 , which covered and clogged the catalyst sites and pores. Moreover, for recovered at 250°C catalyst, the intensity of the bands at 1398 cm^{-1} , 1137 cm^{-1} and 1046 cm^{-1} were further weakened, which suggested that the amount of the NH_4^+ and SO_4^{2-} ions decreased with temperature increasing. In addition, there were no sulfate species bands detected on catalyst recovered at 490°C , which means that the deactivating ammonium sulfate salt agents could be decomposed at 490°C and above. It also demonstrated that there were no any metal sulfates formed by SO_2 at low temperature in the SCR reaction.

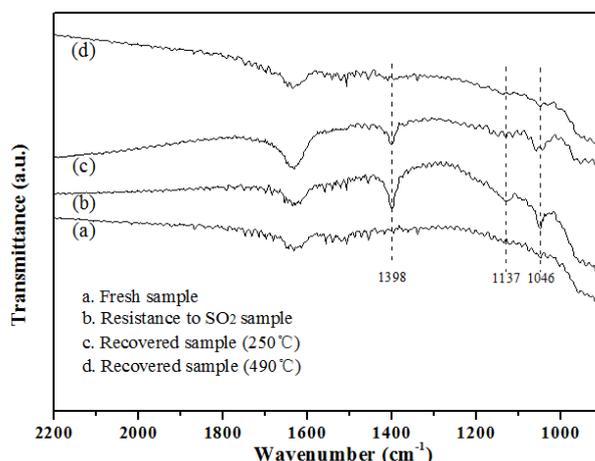


FIG. 5 FT-IR SPECTRA OF POISONED $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ CATALYSTS

The results of thermo stability for poisoned and recovered catalysts are presented in Fig.6. In the first stage before 100 °C, the evident weight loss of samples were resulted from the desorption of physical adsorbed water. For poisoned and recovered at 250 °C catalysts, apart from the weight loss result from H₂O desorption, a new weight loss at the temperature between 200-400 °C were also observed. Such small weight loss could be attributed to the decomposition of ammonium sulfate (Nam I S, 1986). However, the corresponding loss was not detected in fresh and recovered at 490 °C samples, which illustrated that poisoned catalyst could achieve to the original fresh SCR activity after regenerated at 490 °C. The last weight loss between 700-900 °C for all the catalysts was corresponded to the sublimation of tungsten oxide (Jie Dang, 2013).

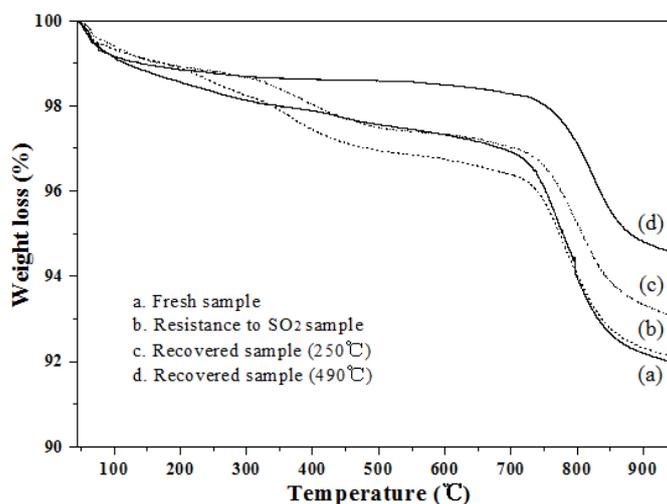


FIG. 6 TG ANALYSES OF POISONED $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ CATALYSTS

4 CONCLUSIONS

The SCR activity between 120-220 °C of the $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ catalyst was greatly improved by TiO_2 surface sulfated with 0.4M H_2SO_4 . It could be affirmed that sulfuric acid doping had positive effect on low-temperature activity of the catalyst. In the presence of 300ppm SO_2 for 50h at 180 °C, the activity of $V_2O_5-WO_3/TiO_2-SO_4^{2-}$ catalyst dropped from 95% to 90%, which was always superior to that of $V_2O_5-WO_3/TiO_2$. The main deactivating substances were ammonium sulfate salts which deactivate the catalyst activity through pore plugging and covering. After calcined at 490 °C, poisoned catalyst could be recovered to the original levels along with ammonium sulfate salt decomposing. This result further ensured that there was no other metal sulfate which decomposed above 490 °C formed in the SCR reaction.

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