Catalytic Performance of Ti³⁺ Self-Doped V₂O₅-TiO₂ Catalysts for Selective Catalytic Reduction with NH₃

Kai Zhang, Wei Zhao*, Shengping Dou, Qian Wang

School of Energy and Power Engineering, Jiangsu University, Zhenjiang, China
Email: *wzhao@ujs.edu.cn

Abstract

Ti³⁺ self-doping modified V_2O_5/TiO_2 catalyst was prepared by sol-gel and impregnation methods and used for selective catalytic reduction (SCR) of NO_x with NH_3. Results showed that Ti³⁺ self-doped V_2O_5/TiO_2 catalyst performed the better catalytic activity. And X-ray diffraction and scanning electron microscopy were used to evaluate the phase composition and morphology of the prepared catalyst. The effects of calcinations temperature of the support, oxygen concentration, $[NH_3]/[NO]$ molar ratio and the GHSV on the denitration performance were investigated. It was found that more than 80% NO_x conversion was obtained at 210°C when the O_2 volume fraction was 5%, the NO concentration was 500 ppm, the $[NH_3]/[NO]$ molar ratio = 1 and the GHSV was 23,885 h^{-1}. The results showed that the catalytic activity increased first with the increasing of O_2 concentration and $[NH_3]/[NO]$ molar ratio, then remained stable. At the same time, the stability of the catalyst was also studied at the temperature of 210°C. The reaction continued for 750 minutes, and the catalytic activity remained above 80%, indicating that the catalyst has a good stability. Moreover, the Ti³⁺ self-doped V_2O_5/TiO_2 catalyst also showed good SO_2 and H_2O resistance. Therefore, these findings provide important information to better understand the application of the prepared catalyst.

Keywords

1. Introduction

Nitrogen oxides (NO_x) are very harmful to the environment and contribute to

acid rain, photochemical smog, ozone depletion and global warming [1]. The selective catalytic reduction (SCR) of NO_x with NH_3 is a well-established and efficient process for the elimination of NO_x emissions [2]. However, the catalyst plays an important role in the SCR system. The activity of the catalyst determines the denitrification efficiency of the SCR system. The commercial catalyst for de-NO_x process is carried out at 350°C - 400°C [3]. With the aim of avoiding the inactivation of the catalyst caused by sulfur dioxide and dust, the SCR equipment is usually installed at the downstream of desulfurization for reducing sulfur dioxide and dust pollution to a minimum [4]. However, the temperature of flue gas from desulfurization is usually low. Therefore, the development of superior low temperature SCR catalysts is getting more and more attention.

For SCR catalysts, V_2O_5/TiO_2 catalysts have attracted much attention due to their low temperature activity and environmental friendliness [5]-[10]. Therefore, the study of modified V_2O_5/TiO_2 catalytic system has great practical significance [11]. In order to improve the activity of the catalyst, many efforts have been paid to modify the material of catalysts. However, the effect of ion doping on the activity of catalyst strongly depends on many factors such as the dopant concentration, the distribution of the dopant, the configuration of doping ions and so on [4]. Zhu *et al.* prepared Nb-doped V_2O_5-WO_3/TiO_2 catalysts for the NH_3-SCR reaction and found the addition of Nb_2O_5 could improve the SCR activity at low temperature. As a result, the thermal treatment at 400°C could regenerate the deactivated catalyst and get SCR activity recovered. The particle and monolith catalysts both kept stable NO_x conversion at 225°C with high concentration of H_2O and SO_2 during the long time tests [12]. Hu *et al.* reported that the dopant of Ce could enhance the surface chemisorbed oxygen on the Na poisoning V_2O_5-WO_3/TiO_2 catalysts, facilitate the redox cycle, and increase the intensity of acid sites due to the newly formed Brønsted acid sites stemmed from Ce^{3+}-NH_4^+, thereby promoting catalytic activity and Na poisoning resistance [13]. Zhao *et al.* found that the S-doped vanadium-titanium catalyst can prevent the phase transition from anatase to rutile, producing crystal defects and reducing the band gap. And the addition of sulfur can bring more NH_3 adsorbent, while increasing the catalytic activity of NO on NH_3-SCR [4]. In order to increase the activity of the catalyst, it is also very necessary to investigate the preparation conditions and reaction conditions. Wang *et al.* experimentally studied Fe_2O_3 particle catalysts in the low temperature selective catalytic reduction (SCR) of NO with NH_3 [14]. The results show that oxygen concentration, $[NH_3]/[NO]$ molar ratio, GHSV and other factors have a great influence on catalytic activity.

In this study, Ti^{3+} self-doped V_2O_5/TiO_2 catalysts were prepared by sol-gel method and impregnation method. The effects of oxygen concentration, $[NH_3]/[NO]$ molar ratio and the GHSV on its performance were investigated. At the same time, the preparation conditions of the support and different doping amount of the Ti^{3+} were investigated.

2. Experimental

2.1. Catalyst Preparation

The titanium dioxide support was prepared by the sol-gel method. Briefly, 12 mL tetrabutyl orthotitanate (98%, TBOT), 48 mL absolute ethanol (AR), 3.8 mL acetylacetone (AR, Hacac) and a certain amount of aluminium acetylacetonate (98%, Al(acac)$_3$) were mixed and stirred for 1 h to obtain solution A while solution B consisted of 60 mL absolute ethanol and 7 mL H$_2$O. Solution B was dropwise added into solution A by titration funnel under magnetic stirring. After stirring for 1 h at room temperature, the sol was heated at 50°C for 4 h in water bath and then subsequently dried at 80°C for 6 h. After that the gel was calcined at 350°C for 2 h in air. Finally, the titanium dioxide support was obtained.

The loading of V$_2$O$_5$ was prepared by impregnation with the requisite amount of ammonium metavanadate (the V$_2$O$_5$ content in all catalysts is 1% by weight). The NH$_4$VO$_3$ was dissolved in 20 mL deionized water at 60°C, and impregnated by contacting the Al-Ti support. The mixture was heated for 4 h at 60°C in a water bath. Then obtained mixture was dried at 120°C for 6 h and calcined at 350°C for 4 h. Samples with different ratios of Ti^{3+} were sighed as x-VTi which x represented the molar percentage of Al(acac)$_3$ to TBOT.

2.2. Characterization of Catalysts

Powder X-ray diffraction (XRD) patterns of all samples were obtained on a XD-3 diffractometer with Cu Ka radiation (k = 0.15418 nm) (Beijing Purkinje General Instrument Co., Ltd., China) operated at 36 kV and 30 mA. Intensity data were reported in the 2θ range from 10° to 80°, with a step size of 0.04°.

Scanning electron microscopy (SEM) produced by Hitachi was used to observe the morphologies of catalysts under the accelerating voltage of 15 kV.

2.3. Catalytic Activity Measurement

Experiments to investigate the catalytic activity of the catalyst were carried out in a fixed-bed flow reactor at 120°C - 330°C containing 0.30 g catalyst under atmospheric pressure. The reactor was heated by a temperature-controlled furnace. They were used to control the gas flow of mass flowmeters. The total gas flow rate was 100 mL/min. The reaction gas components were as follows: 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$ and balanced N$_2$. The gas hourly space velocity was 23,885 h^{-1}. Different space velocities were obtained by changing the gas total flow or the volume of catalyst used. The mixed gas went into the reactor and the NO and NO$_2$ (NO$_X$ = NO + NO$_2$) concentrations were monitored by a Testo350 flue gas analyzer (Testo, Germany). The reaction system was kept for 1 h at each reaction temperature to reach a steady state before the analysis of the outlet gas was performed. The NO$_X$ conversion could be defined as Equation (1):

$$X_{NO_X} = \frac{[NO_X]_{in} - [NO_X]_{out}}{[NO_X]_{in}} \tag{1}$$

There $[NO_X]_{in}$ and $[NO_X]_{out}$ represent the concentrations of NO_X in the inlet and outlet gas stream respectively.

3. Results and Discussion

3.1. Activity of Catalyst

The activity of different Ti^{3+} doping amount is tested, and the results are shown in **Figure 1**. The denitration activity of all Ti^{3+} self-doped V_2O_5/TiO_2 catalysts increased with the increase of temperature. Compared with the 0-VTi catalyst, the activity efficiency is significantly improved. The catalytic activity of 0.2-VTi was the highest, and reached 88% at 210°C. Therefore, when the $Al(acac)_3/TBOT$ ratio is 0.2%, Ti^{3+} self-doping has the best effect on the catalyst.

The XRD patterns of the prepared catalysts are shown in **Figure 2**. It can be seen from **Figure 2** that the sample after Ti^{3+} self-doping (the 0.2-VTi catalyst) shows the major crystalline phase of anatase TiO_2. However, the 0-VTi catalyst shows trace amount of rutile phase. This indicates that the Ti^{3+} doping can inhibit the formation of rutile phase. In addition, there is no characteristic peak of V_2O_5 was detected, indicating that V element may be well dispersed on the catalyst surface [15] [16].

Figure 3 shows the SEM images of the synthesized 0.2-VTi catalyst sample. SEM image shows that the composite consists of irregular shaped aggregates. **Figure 3** shows there is no obvious change of structure between fresh catalyst (**Figure 3(a)**) and used catalyst (**Figure 3(b)**). Moreover, no single V_2O_5 particles or clusters were found on the surface of TiO_2. This indicates that V_2O_5 species may cover the surface of TiO_2 particles in the form of a single thick layer. This is consistent with the results of XRD [17].
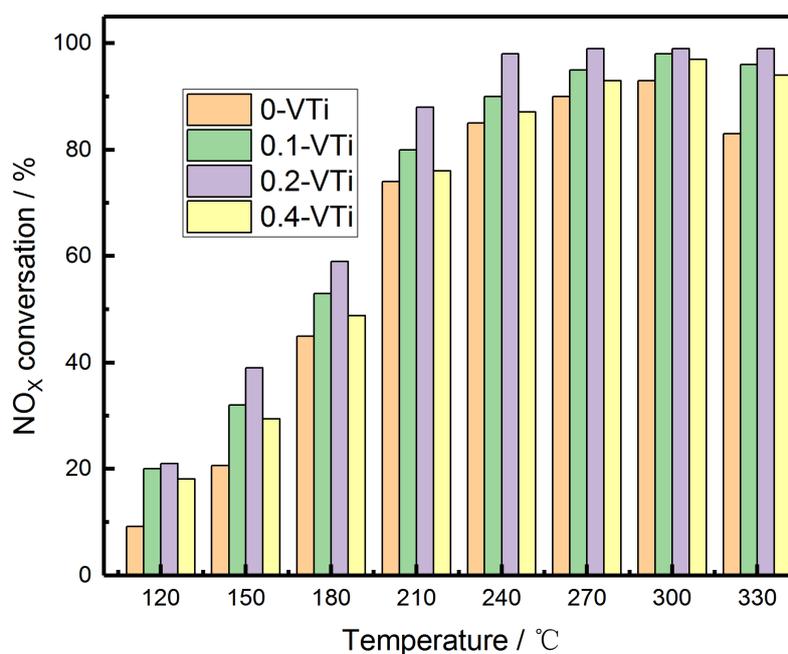
Figure 1. Effect of Ti^{3+} self-doped V_2O_5/TiO_2 catalyst on NO_X conversation.
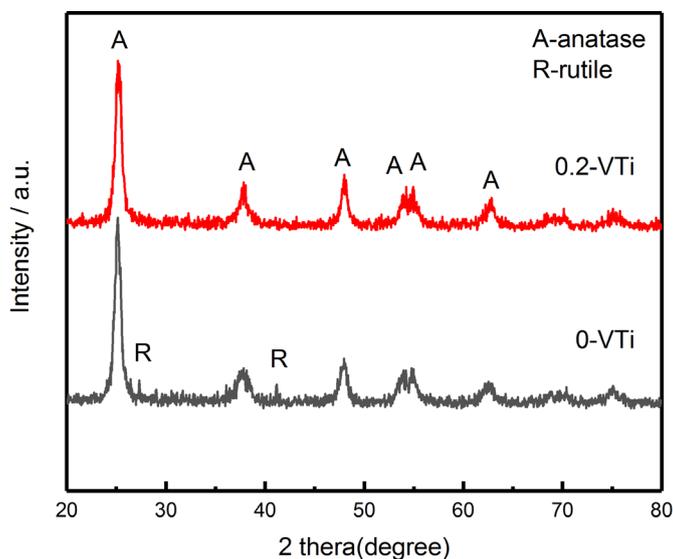
**Figure 2.** XRD patterns of the catalysts with various Ti³⁺ doping.
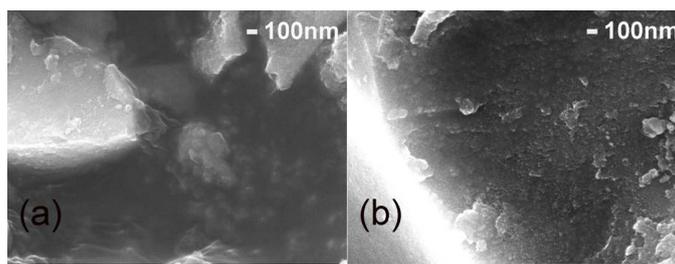
Figure 3. SEM micrographs of the 0.2-VTi catalyst, (a) fresh, (b) used.

3.2. Effect of the Calcined Temperature of the Support on SCR Activity

Figure 4 shows the NO_x conversion as a function of temperature (from 120˚C to 330˚C) in the NH_3-SCR reaction over Ti³⁺ self-doped V_2O_5/TiO_2 catalysts of the different calcined temperature of the support. From the result, it was clear to be found that the NO_x conversion is the highest when the support calcinations temperature is 350˚C. It presented an over 80% NO_x conversion within the temperature range of 200˚C - 330˚C, especially at 240˚C - 330˚C where the NO_x conversion was increased to a maximum of exceed 99%. However, the catalytic activity at low temperature calcinations is relatively low. This may be because the low temperature calcined catalyst has a low degree of crystallinity [18]. And in appearance, the support prepared at a low temperature appeared black, because of incomplete calcinations and residual carbon, resulting in low denitrification efficiency. It can also be seen from **Figure 4** that the catalytic activity declines when the support was calcined at high temperatures.

3.3. Effect of O₂ Concentration on SCR Activity

It was found through previous studies that oxygen is very important for SCR of
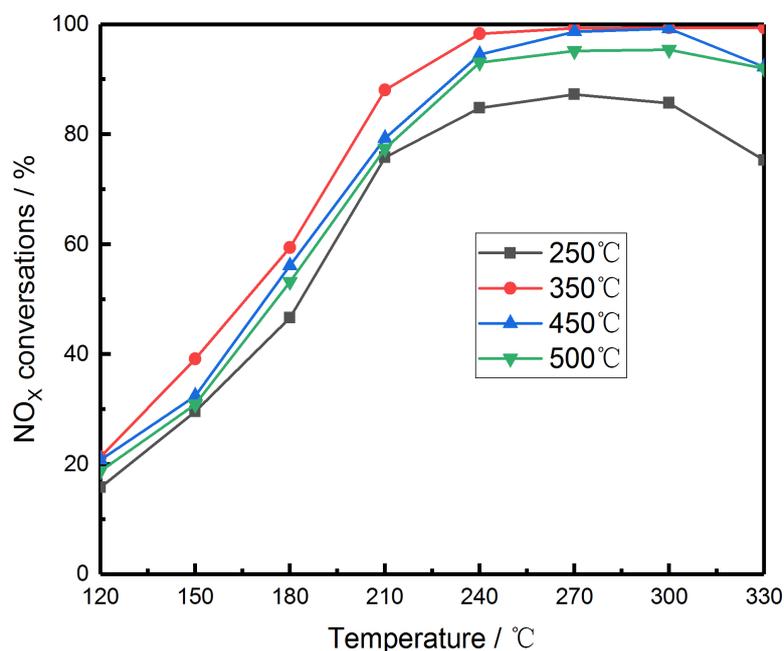
Figure 4. Effect of Ti^{3+} catalysts of various calcined temperature of the support. Reaction conditions: $[NO]$ = $[NH_3]$ = 500 ppm, O_2 = 5%, balance N_2, GHSV = 23,885 h^{-1}, total flow rate 100 mL/min.

NO with NH$_3$ at low temperature [19]. **Figure 5** shows the effect of oxygen concentration on SCR activity at 210˚C. It was clear that the NO$_x$ conversion over the catalyst increased with the increasing of oxygen concentration, especially when the oxygen concentration was less than 3%. The 36% NO$_x$ conversion was obtained in the presence of without O$_2$ at 210˚C. This indicates that the catalyst has the ability to catalyze and reduce in the absence of O$_2$. However, the NO$_x$ conversion increases significantly as the O$_2$ concentration increased to 3%. This shows that O$_2$ has a great influence on the catalytic activity. The NO$_x$ conversion increased to 88.1% when O$_2$ reached 5%. However, the catalytic activity remained basically stable with the continued increase of O$_2$ concentration. Therefore, the optimal O$_2$ concentration is 5%.

3.4. Effect of the [NH$_3$/NO] Molar Ratio on SCR Activity

It is well known that the [NH$_3$]/[NO] molar ratio is a key parameter in SCR of NO with NH$_3$ [14]. **Figure 6** shows the effect of different [NH$_3$/NO] molar ratio on catalytic activity at 210˚C. It can be clearly seen that the catalytic activity changes significantly when the molar ratio of [NH$_3$]/[NO] is less than one, and the activity rose rapidly as the [NH$_3$]/[NO] molar ratio increases. When the [NH$_3$]/[NO] molar ratio is 1, the catalytic activity reached over 88%. However, the NO$_x$ conversion varied more gradually when a higher molar ratio of [NH$_3$]/[NO] was used. The continued increase of the NH$_3$ concentration will not increase the NO$_x$ conversion. Therefore, the [NH$_3$]/[NO] molar ratio of 1 is advisable for this experiment.
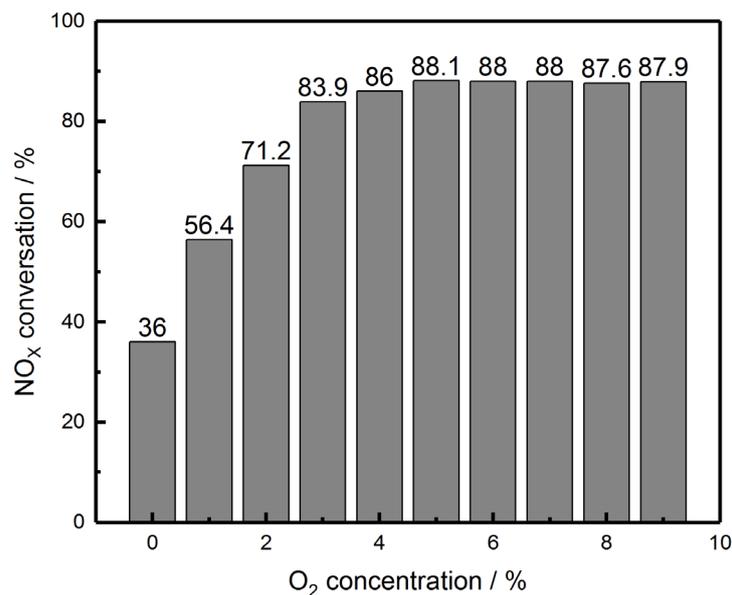
Figure 5. Effect of the O_2 concentration on catalytic activity at 210˚C. Reaction conditions: [NO] = [NH_3] = 500 ppm, balance N_2, GHSV = 23,885 h^{-1}, total flow rate 100 mL/min.
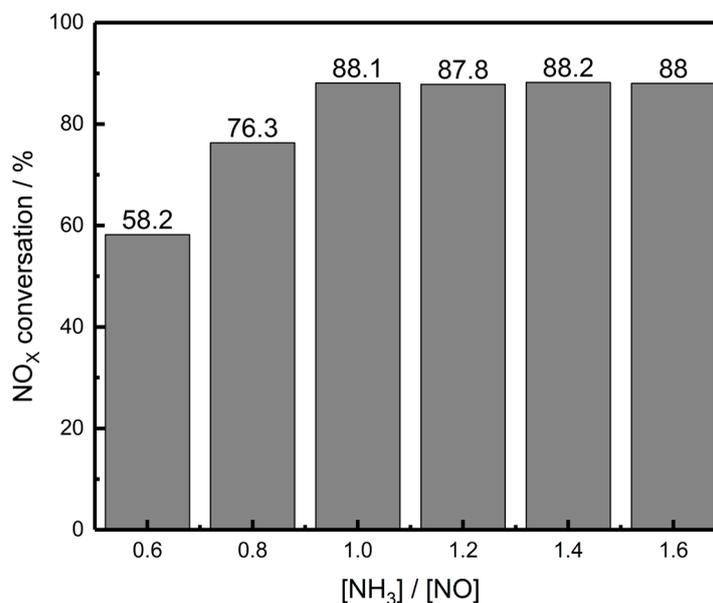
Figure 6. Effect of [NH_3]/[NO] molar ratio on catalytic activity at 210˚C. Reaction conditions: [NO] = 500 ppm, O_2 = 5%, GHSV = 23,885 h^{-1}, balance N_2, total flow rate 100 mL/min.

3.5. Effect of GHSV on SCR Activity

The GHSV is an important parameter that has a great influence on the denitrification efficiency of SCR catalysts. This work also measured the effect of GHSV on SCR activity, as shown in **Figure 7**. It can be clearly seen that the catalytic activity decreases with the increasing of GHSV. And the catalytic activity was the best at 23,885 h^{-1}, in particular, the catalytic activity reached 88.1% at 210˚C and
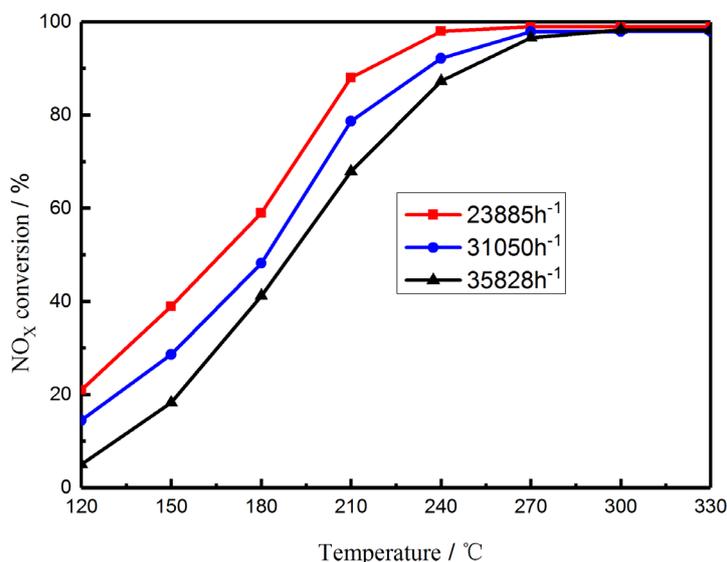
Figure 7. Effect of GHSV on catalytic activity. Reaction conditions: balance N_2, total flow rate are 23,885 h^{-1}, 31,050 h^{-1} and 35,828 h^{-1} respectively.

the activity exceeded 99% between 240°C - 330°C. This is because when the GHSV is too high, the contact time between the reactants and the catalyst is short and the reaction is not sufficient, the conversion rate is low.

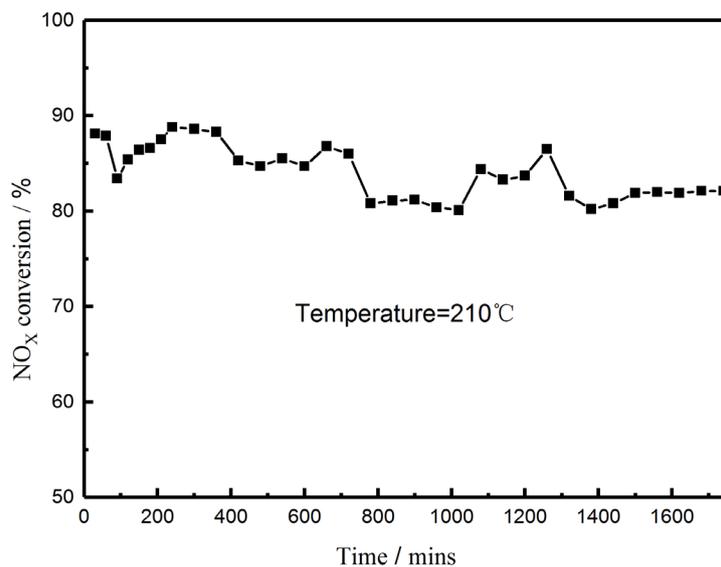### 3.6. Effect of the Reaction Time on SCR Activity

In order to evaluate the stability of the catalytic activity, a comprehensive experiment was carried out at a standard reaction of catalyst activity test at 210°C. The results are shown in Figure 8. It was found that the NO conversion was always kept over 80% for the catalyst continued to react for over 1750 min·s, indicating that the catalyst had better activity and stability.
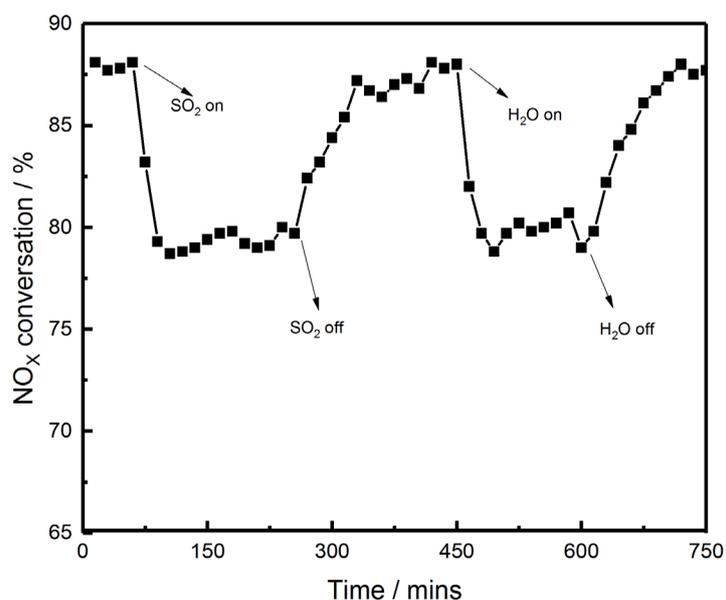
3.7. Effect of H₂O and SO₂ on SCR Activity

Sulfur dioxide as another important pollution was in the flue gas inevitably [12]. The effect of H_2O and SO_2 on the activity of the catalyst was investigated experimentally at 210°C, and the result is exhibited in Figure 9. When the 500 ppm SO_2 was added in firstly, the obvious decrease of NO conversion was not observed. The NO_x conversion decreased from 88.1% to about 78% after a 250 min·s 'SCR reaction process. When the supply of SO_2 was cut off at 250 min, NO_x concentration in the exhaust recovered gradually to the original level. Then 5% H_2O was introduced at 450 min, and the experimental results showed that the NO_x conversion decreased rapidly. When the H_2O is turned off at 600 min, the NO_x conversion is quickly restored. Therefore, Ti^{3+} self-doped V_2O_5/TiO_2 catalyst has superior SO_2 and H_2O resistance.

4. Conclusion

On the basis of the above results, it can be concluded that the catalytic activity of

Figure 8. Effect of reaction time on catalytic activity at 210˚C. Reaction conditions: [NO] = 500 ppm, O_2 = 5%, GHSV = 23,885 h^{-1}, balance N_2, total flow rate 100 mL/min.

Figure 9. Effect of H_2O and SO_2 on catalytic activity at 210˚C. Reaction conditions: [NO] = 500 ppm, O_2 = 5%, SO_2 = 500 ppm, H_2O = 5%, GHSV = 23,885 h^{-1}, balance N_2, total flow rate 100 mL/min.

V_2O_5/TiO_2 catalyst at low temperature is significantly affected by the self-doping of Ti^{3+}, which can reach up to 80% at 200˚C. The investigation showed that the activity of the catalyst is the best when the oxygen concentration is 5% and the [NH_3]/[NO] molar ratio is 1. At the same time, the effect of GHSV on the catalyst is investigated. It is found that the catalyst also has a wide active range at a large GHSV. In addition, the experimental results showed that the Ti^{3+} self-doped V_2O_5/TiO_2 catalyst has good stability and better SO_2 and H_2O resis-

tance during a long time.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Zhu, J. and Thomas, A. (2009) Perovskite-Type Mixed Oxides as Catalytic Material for NO Removal. *Applied Catalysis B: Environmental*, **92**, 225-233. https://doi.org/10.1016/j.apcatb.2009.08.008

[2] Liu, J., Li, X., Zhao, Q., Ke, J., Xiao, H., Lv, X., Liu, S., Tadé, M. and Wang, S. (2017) Mechanistic Investigation of the Enhanced NH_3-SCR on Cobalt-Decorated Ce-Ti Mixed Oxide: *In Situ* FTIR Analysis for Structure-Activity Correlation. *Applied Catalysis B: Environmental*, **200**, 297-308. https://doi.org/10.1016/j.apcatb.2016.07.020

[3] Busca, G., Lietti, L., Ramis, G. and Berti, F. (1998) Chemical and Mechanistic Aspects of the Selective Catalytic Reduction of NOx by Ammonia over Oxide Catalysts: A Review. *Applied Catalysis B: Environmental*, **18**, 1-36. https://doi.org/10.1016/S0926-3373(98)00040-X

[4] Zhao, W., Zhong, Q., Pan, Y. and Zhang, R. (2013) Systematic Effects of S-Doping on the Activity of V_2O_5/TiO_2 Catalyst for Low-Temperature NH_3-SCR. *Chemical Engineering Journal*, **228**, 815-823. https://doi.org/10.1016/j.cej.2013.05.056

[5] Youn, S., Song, I., Lee, H., Cho, S.J. and Kim, D.H. (2018) Effect of Pore Structure of TiO_2 on the SO_2 Poisoning over V_2O_5/TiO_2 Catalysts for Selective Catalytic Reduction of NO_x with NH_3. *Catalysis Today*, **303**, 19-24. https://doi.org/10.1016/j.cattod.2017.08.015

[6] Kim, J.H., Choi, J.H. and Phule, A.D. (2018) Development of High Performance Catalytic Filter of V_2O_5-WO_3/TiO_2 Supported-SiC for NO_x Reduction. *Powder Technology*, **327**, 282-290. https://doi.org/10.1016/j.powtec.2017.12.081

[7] Wang, C., Li, X., Yuan, Y., Wang, B., Huang, J., Xia, F., Zhang, H. and Xiao, J. (2017) Effects of Sintering Temperature on Sensing Properties of V_2O_5-WO_3-TiO_2 Electrode for Potentiometric Ammonia Sensor. *Sensors and Actuators B: Chemical*, **2412**, 68-275. https://doi.org/10.1016/j.snb.2016.09.117

[8] Kompio, P.G.W.A., Brückner, A., Hipler, F., Manoylova, O., Auer, G., Mestl, G. and Grünert, W. (2017) V_2O_5-WO_3/TiO_2 Catalysts under Thermal Stress: Responses of Structure and Catalytic Behavior in the Selective Catalytic Reduction of NO by NH_3. *Applied Catalysis B: Environmental*, **217**, 365-377. https://doi.org/10.1016/j.apcatb.2017.06.006

[9] Chen, M., Zhao, M., Tang, F., Ruan, L., Yang, H. and Li, N. (2017) Effect of Ce Doping into V_2O_5-WO_3/TiO_2 Catalysts on the Selective Catalytic Reduction of NO_x

by NH_3. *Journal of Rare Earths*, **35**, 1206-1215.
https://doi.org/10.1016/j.jre.2017.06.004

[10] Aguilar-Romero, M., Camposeco, R., Castillo, S., Marín, J., Rodríguez-González, V., García-Serrano, L.A. and Mejía-Centeno, I. (2017) Acidity, Surface Species, and Catalytic Activity Study on V_2O_5-WO_3/TiO_2 Nanotube Catalysts for Selective NO Reduction by NH_3. *Fuel*, **198**, 123-133. https://doi.org/10.1016/j.fuel.2016.11.090

[11] Zhang, S., Zhong, Q., Zhao, W. and Li, Y. (2014) Surface Characterization Studies on F-Doped V_2O_5/TiO_2 Catalyst for NO Reduction with NH_3 at Low-Temperature. *Chemical Engineering Journal*, **253**, 207-216. https://doi.org/10.1016/j.cej.2014.04.045

[12] Zhu, L., Zhong, Z., Xue, J., Xu, Y., Wang, C. and Wang, L. (2018) NH_3-SCR Performance and the Resistance to SO_2 for Nb Doped Vanadium Based Catalyst at Low Temperatures. *Journal of Environmental Sciences* (*China*), **65**, 306-316. https://doi.org/10.1016/j.jes.2017.06.033

[13] Hu, G., Yang, J., Tian, Y., Kong, B., Liu, Q., Ren, S., Li, J. and Kong, M. (2018) Effect of Ce Doping on the Resistance of Na over V_2O_5-WO_3/TiO_2 SCR Catalysts. *Materials Research Bulletin*, **104**, 112-118. https://doi.org/10.1016/j.materresbull.2018.04.009

[14] Wang, X.B. and Gui, K. (2013) Fe_2O_3 Particles as Superior Catalysts for Low Temperature Selective Catalytic Reduction of NO with NH_3. *Journal of Environmental Sciences*, **25**, 2469-2475. https://doi.org/10.1016/S1001-0742(12)60331-3

[15] You, Y., Ito, A., Tu, R. and Goto, T. (2013) Preparation of the c-Axis Oriented AlN Film by Laser Chemical Vapor Deposition Using a Newly Proposed $Al(acac)_3$ Precursor. *Journal of Crystal Growth*, **365**, 1-5. https://doi.org/10.1016/j.jcrysgro.2012.12.034

[16] Gao, X., Zhang, F., Yu, Y., Dou, Y., Xu, L. and Liu, G. (2019) Effect of Mo Loading on 2-Naphthaldehyde Formation from Vapor Phase Oxidation of 2-Methylnaphthalene with V_2O_5/TiO_2 Catalysts. *Catalysis Communications*, **122**, 47-51. https://doi.org/10.1016/j.catcom.2018.12.019

[17] Zhao, W., Dou, S., Zhang, K., Wu, L., Wang, Q., Shang, D. and Zhong, Q. (2019) Promotion Effect of S and N Co-Addition on the Catalytic Performance of V_2O_5/TiO_2 for NH_3-SCR of NOX. *Chemical Engineering Journal*, **364**, 401-409. https://doi.org/10.1016/j.cej.2019.01.166

[18] Xie, Z., Wang, F., Liang, J., Wang, Z., Hui, N. and Ding, Y. (2018) Enhanced Catalytic Efficiency of $FeMnTiO_x$ SCR Catalysts through Adding Tourmaline Nanopowders during the One-Step Sol-Gel Process. *Materials Letters*, **217**, 60-63. https://doi.org/10.1016/j.matlet.2018.01.013

[19] Xu, W., Wang, H., Zhou, X. and Zhu, T. (2014) CuO/TiO_2 Catalysts for Gas-Phase Hg^0 Catalytic Oxidation. *Chemical Engineering Journal*, **243**, 380-385. https://doi.org/10.1016/j.cej.2013.12.014