

F-Doped V₂O₅-WO₃/TiO₂ as a Catalyst for NO Reduction with NH₃ at Low-Temperature

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Abstract—A F- and W- doped V₂O₅/TiO₂ has been developed used for low-temperature selective catalytic reduction (SCR) of NO with ammonia. The experimental results showed that NO conversion could be improved by doping F and W, NH₃ and O₂ were important for the NO adsorption over the VWTiF catalyst and the VWTiF catalyst had a good SO₂ and H₂O resistance.

Intex Terms—F- and W- doped V₂O₅/TiO₂; SCR.

I. INTRODUCTION

Nitrogen oxides (NO_x) are very harmful for the ecosystem and humanity [1]. It contributes to photochemical smog, acid rain, ozone depletion and greenhouse effect [2]. The selective catalytic reduction (SCR) of NO_x with NH₃ in the presence of excess oxygen has been proven to be an efficient process for the removal of NO_x from stationary sources [3-5]. The industrial operations are carried out at 350-400 °C [6, 7]. However, the high concentration of ash (e.g. K₂O, CaO and As₂O₃) in the flue gas reduces their performance and longevity at this temperature [7, 8]. In addition, the high temperature may cause side reactions, such as oxidation of NH₃ into NO and formation of N₂O. However, this could be avoided by locating the SCR unit downstream of the precipitator and even downstream of desulfurizer, through the development of a low temperature (<250 °C) SCR.

Recently, most of the researches of SCR at low temperature focus on manganese oxides due to their high catalytic activities at low-temperature [9-12], such as Mn-Fe [7], Mn-Ce [13, 14], Mn-Cu [15]. However, MnO_x sites can form MnSO₄ in the presence of SO₂ to result in the deactivation of the catalysts [16]. Commercial catalyst V₂O₅ + WO₃ / TiO₂ has been applied for many years and has a strong SO₂ resistance, but the operations are carried out at high temperature.

In our previous study [17], we proposed a novel F-doped V₂O₅-WO₃/TiO₂ catalyst for lower temperature SCR. It was found that the reduced WO₃ can be oxidized by oxygen and oxygen may be reduced to superoxide ions. The superoxide ions over the catalysts are one of the ways to improve the activity of low-temperature SCR of NO with NH₃. Therefore, the aim of this study is to improve the catalyst formulation

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and to investigate the impact of O₂, NH₃, SO₂ and H₂O on the catalytic performance. In this study, we found that VW₃TiF_{1.5} was the best catalyst and this catalyst had a good SO₂ and H₂O resistance. The information in this paper would contribute to a better understanding of the low-temperature SCR processes over F-doped V₂O₅-WO₃/TiO₂ catalyst.

II. EXPERIMENTAL

A. Catalyst Preparation

The F-doped V₂O₅-WO₃/TiO₂ catalyst was prepared by a sol-gel method for F-doped titania preparation, followed by impregnation for W and then V, specifically as follows: Ti(OC₄H₉)₄ (0.064 mol) was stabilized by adding 0.128 mol acetylacetone. A color change of the solution from pale yellow to orange occurred under continuous stirring. The solution was diluted with 50mL (NH₄)₂TiF₆ (0.864 mmol) ethanolic solutions. After stirring for 2 h at room temperature, the sol was concentrated in a 60 °C water bath and subsequently dried at 120 °C for 6 h. The gel was calcined at 500 °C for 3h in air. The F/Ti molar ratio was 1.35×10⁻², and it is further referred to as TiF. After impregnation in ammonium wolframate solution (WO₃ doping was 3%) in a 60 °C water bath and refluxing for 4 h, the sieved TiF was dried at 120 °C for 6h and subsequently calcined at 500 °C for 2 h. It was further referred to as WTiF. The ammonium metavanadate (V₂O₅ loading was 1%) was first dissolved in 50 ml deionized water at 80 °C. Then the WTiF was added under conditions of constant temperature and stirring. After 1 h, the mixture was dried at 120 °C for 6 h and subsequently calcined at 500 °C for 2 h. Finally, the F- and W- doped V₂O₅/TiO₂ catalyst was obtained and it was further referred to as VWTiF.

B. Catalytic Activity Tests

The SCR of NO was carried out at 120-240 °C in a fixed-bed flow reactor (i.d. 6.8 mm) containing catalyst sample (100-120 mesh) under atmospheric pressure. The gas flow was controlled by mass flow meters. The reaction temperature was measured by a type K thermocouple inserted into the catalyst bed. The reactant gas consisted of 500 ppm NO, 500 ppm NH₃, 3% O₂ and balanced N₂. Each catalyst sample was adsorbed by the reaction mixture before the reaction for avoiding errors caused by NO adsorption on the catalyst. All of the catalysts were kept on stream at each temperature for 1 h. The NO concentration in the inlet and outlet gas was measured by a MRU Vario Plus flue gas analyzer (Germany) and N₂O was monitored by GHX-510 IR gas analyzer (China).

III. RESULTS AND DISCUSSION

A. Catalytic Activity Tests

Fig. 1 shows the comparison of catalytic performance of different kind of prepared catalysts (VWTiF, VTiF, VWTi and VTi) as a function of temperature from 120 to 240 °C. As we can see the SCR activity at low temperatures decreased in this following order: VWTiF > VTiF > VWTi > VTi. VTi showed low catalytic activity at 120 -240 °C and the NO conversion increased slowly with the rise of temperature. VTiF and VWTi had a higher NO conversion than VTi, but the NO conversion of VTiF and VWTi were 53.9% and 52.3%, respectively. For the VWTiF catalyst, a clearly promotional impact was obtained and NO conversion of VWTiF catalyst increased significantly with increasing temperature.

B. Effect of F Doping and W Loading on NO Conversion

The effect of VWTiF catalysts of different F doping is displayed in Fig. 2. F doping significantly enhanced the NO conversion, and when F/Ti molar ratio was 1.35%, the catalyst had highest catalytic activity. This result is in good agreement with our previous study [18]. The effect of various W loadings from 0 to 5% on the performance of the VWTiF catalyst is shown in Fig. 3. NO conversion was improved with the increase of W loading. It is worth noting that, when the WO_3 content was 5%, the VW_5TiF catalyst showed almost the same activity as VW_3TiF (VWTiF).

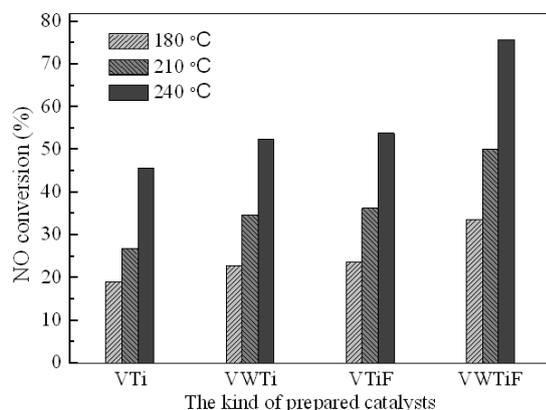


Fig. 1. Comparison of catalytic performance of different kind of prepared catalysts (VWTiF, VTiF, VWTi and VTi). Reaction conditions: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , N_2 as balance gas, GHSV=43,000 h^{-1} .

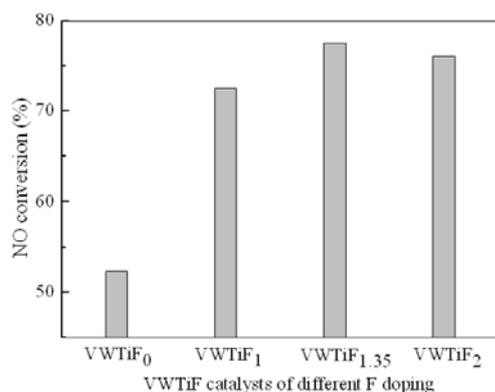


Fig. 2. Effect of VWTiF catalysts of different F doping. Reaction conditions: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , N_2 as balance gas, GHSV=43,000 h^{-1} .

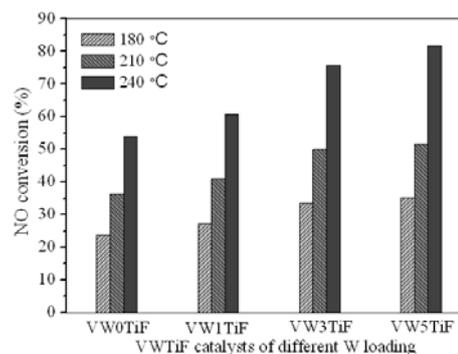


Fig. 3. Effect of VWTiF catalysts of various W loadings. Reaction conditions: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , N_2 as balance gas, GHSV=43,000 h^{-1} .

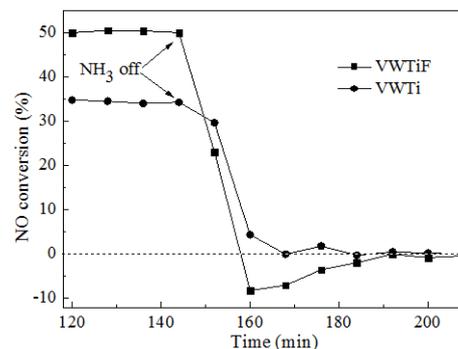


Fig. 4. Transient experiments: the effect of NH_3 on NO conversion of VWTiF and VWTi. Reaction conditions: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , N_2 as balance gas, GHSV=43,000 h^{-1} , $T=210$ °C.

 C. Transient Experiments of Effect of NH_3 on NO Conversion

Our previous studies found that the interaction between WO_3 and TiO_2 by F doping improved the superoxide ions formation and NH_3 provided electrons for the superoxide ions formation [17]. It could also be noticed that superoxide ions over SCR catalysts was important to enhance the formation of nitro and nitrate groups which were the intermediates that react with adsorbed ammonia for SCR process at low temperatures [19]. Therefore, NH_3 is important to the VWTiF catalyst. Fig. 4 shows the transient experiments: the effect of NH_3 on NO conversion of VWTiF and VWTi. When the NH_3 supply was switched off, the NO conversion of VWTiF and VWTi decreased. The NO conversion of VWTiF decreased more clearly than VWTi and the macroscopic NO conversion became negative value (The NO concentration of outlet of fixed-bed flow reactor was more than the inlet), however, the NO conversion of VWTi decreased directly to 0%. It indicated that NH_3 was important to the NO adsorption and there was more NO adsorption of the VWTiF catalyst than the VWTi. It was good for the SCR process at low temperatures.

 D. Effect of O_2 Concentration on NO Conversion

It was known from previous studies [20, 21] that O_2 had significant effect on SCR performance. In this paper, the effect of O_2 concentration on NO conversion of VWTiF has been studied and shows in Fig. 5. The NO conversion was stable as the O_2 concentration in 10%-5% and the conversion decreased slightly when the O_2 concentration was 3%. At low O_2 concentration, the NO conversion decreased sharply to

62.6% and 45.9% when the O₂ concentration was 1% and 0%, respectively. As the O₂ concentration increased from 0% to 5%, the original efficiency of SCR reaction was restored in several minutes. When the O₂ supply was switched on the NO instantaneous conversion was not restored immediately to original efficiency, but it increased to 88.4% quickly and then decreased to 75.6% (original efficiency) by degrees in 20 minutes (displayed in the inset of Fig. 4). The reason of this result was that O₂ promoted the NO adsorption over VWTiF so that the NO concentration of outlet of fixed-bed flow reactor decreased.

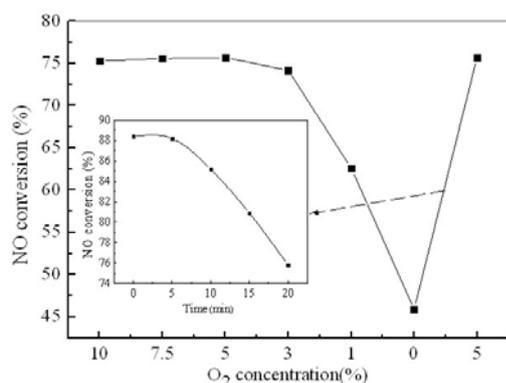


Fig. 5. The effect of O₂ concentration on NO conversion of VWTiF. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, N₂ as balance gas, GHSV=43,000 h⁻¹, T=240 °C.

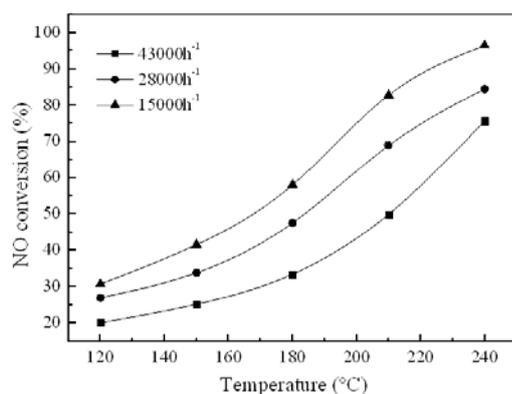


Fig. 6. The catalytic activity of VWTiF in a range of GHSV from 15,000 to 43,000 h⁻¹. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, N₂ as balance gas.

E. Effect of GHSV on NO Conversion

The space velocity is very important for practical applications. Fig. 6 is catalytic activity of VWTiF in a range of GHSV from 15,000 to 43,000 h⁻¹. As shown in Fig. 6, the NO conversion increased clearly as GHSV decreased. When the GHSV reached 15,000 h⁻¹, VWTiF had an excellent NO conversion that was 82.8% at 210 °C and almost no NO could be detected in outlet of fixed-bed flow reactor at 240 °C. The formation of N₂O was <3 ppm under our testing conditions, and thus the selectivity to N₂ was promising.

F. SO₂ and H₂O Resistance for the VWTiF Catalyst

Fig. 7 shows the evolution of NO conversion in the present of H₂O, 300 ppm SO₂ and H₂O+300 ppm SO₂ with time on stream at 210°C and 240°C. The NO conversion immediately decreased when the 4% H₂O switched on at 210°C. When the

reaction temperature up to 240°C, adding 4% H₂O had almost no influence on NO conversion, and adding 6% H₂O, the NO conversion gradually decreased again. It indicated that H₂O inhibition decreased with increasing reaction temperature and the higher H₂O concentration could increase the inhibition. After the H₂O off, the NO conversion immediately decreased. This may be due to capillary condensation of H₂O in the catalyst pore and it prevented the adsorption of NH₃ and NO. After a period of time, the catalytic activity gradually recovered and NO conversion recovered more quickly at 240°C. When SO₂ was added, NO conversion increased slightly. After 15 min the NO conversion gradually decreased and finally stabilized. The NO conversion had no influence by increasing the concentration of ammonia from 500 to 600 ppm (as shown in Fig. 7, point “A”). It indicated that the reason of catalytic activity decrease was the sulfate species deposited on catalyst surface and catalytic active center was covered. When both H₂O and SO₂ were added, the inhibition was more severe than the sum of inhibitions observed when H₂O and SO₂ were added individually, indicating a synergistic inhibitory effect of H₂O and SO₂. This synergistic inhibition was recovered and NO conversion recovered more quickly at 240°C when the H₂O and SO₂ were removed from the reaction mixture.

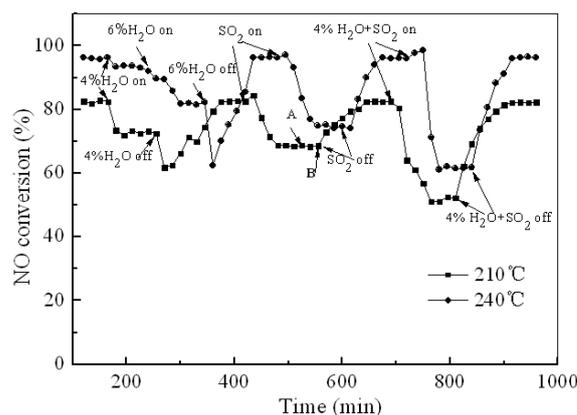


Fig. 7. Evolution of NO conversion in the present of H₂O, 300 ppm SO₂ and H₂O+300 ppm SO₂ with time on stream at 210°C and 240°C: (a) NO conversion at 210°C, (b) NO conversion at 240°C, GHSV=15,000 h⁻¹, Point “A” changing ammonia concentration from 500 to 600ppm, Point “B” changing back ammonia concentration from 600 to 500ppm.

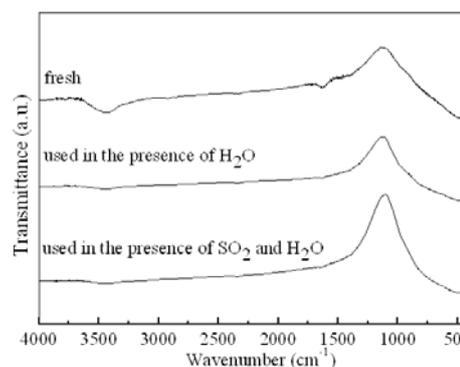


Fig. 8. FT-IR spectra of the fresh and used catalysts

FT-IR spectra of the fresh and used catalysts are both present in Fig. 8. The main bands were located at 400-700 cm⁻¹, and were attributed to the Ti-O stretching and Ti-O-Ti bridging stretching modes [22]. Chen and Yang [23] had

reported that SO_4^{2-} possessed a Td symmetric characteristic, which showed two IR adsorption peak at 1104 and 613 cm^{-1} . After the SCR reaction in the presence of $\text{SO}_2 + \text{H}_2\text{O}$, the IR spectra had no variety mainly in this range. Therefore, the VWTiF catalyst had a good SO_2 resistance.

IV. CONCLUSION

The catalytic activity of NO removal was obviously enhanced on the F-doped $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts for low-temperature SCR of NO with NH_3 . NH_3 and O_2 were important for the NO adsorption over the VWTiF catalyst and the VWTiF catalyst had a good SO_2 and H_2O resistance. VWTiF catalyst with the molar ratio of F/Ti reached 1.35% and 3% WO_3 loadings showed the best activity.

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