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Q3 NH₃-SCR performance and the resistance to SO₂ for Nb doped 2 vanadium based catalyst at low temperatures

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A B S T R A C T

Niobium oxide as the promoter was doped in the V/WTi catalyst for the selective catalytic 17
 reduction (SCR) of NO. The results showed that the addition of Nb₂O₅ could improve the SCR 18
 activity at low temperatures and the 6 wt.% additive was an appropriate dosage. The 19
 enhanced reaction activity of adsorbed ammonia species and the improved dispersion of 20
 vanadium oxide might be the reasons for the elevation of SCR activity at low temperatures. 21
 The resistances to SO₂ of 3V6Nb/WTi catalyst at different temperatures were investigated. 22
 FTIR spectrum and TG-FTIR result indicated that the deposition of ammonium sulfate 23
 species was the main deactivation reason at low temperatures, which still exhibited the 24
 reactivity with NO above 200°C on the catalyst surface. There was a synergistic effect among 25
 NH₃, H₂O and SO₂ that NH₃ and H₂O both accelerated the catalyst deactivation in the 26
 presence of SO₂ at 175°C. The thermal treatment at 400°C could regenerate the deactivated 27
 catalyst and get SCR activity recovered. The particle and monolith catalysts both kept stable 28
 NO_x conversion at 225°C with high concentration of H₂O and SO₂ during the long time tests. 29

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43 Introduction

46 Along with the emergence of air environmental problem, the 47
 regulations of the emission levels in China are becoming more 48
 and more stringent (Liang et al., 2011; Ma and Takeuchi, 2017). 49
 Nitrogen oxides generated by stationary source are a kind of 50
 main atmospheric pollutant, which has been paid a lot atten- 51
 tion to for many years (Roy et al., 2009). Selective catalytic 52
 reduction (SCR) of NO_x by ammonia is the most efficient and 53
 ripest technology for NO_x control of coal-fired power plants. 54
 However, the relatively high operation temperature window 55
 (300–400°C) is the great obstacle for the application of the 56
 commercial V₂O₅-WO₃(MoO₃)/TiO₂ in the industrial boiler,

such as grate furnaces and rotary kiln. Therefore, a lot of 57
 researchers focused on developing a new kind of SCR catalyst 58
 for NO_x removal of industrial environment at low tempera- 59
 tures (Li et al., 2011; Fu et al., 2014; Chen et al., 2014; Shan and 60
 Song, 2015). Low application temperature could let the SCR 61
 reactor install behind the dust precipitator avoiding the fly 62
 ash abrasion, blocking, poisoning and increasing the lifetime 63
 of catalyst. 64

Niobium in the same main group with vanadium has been 65
 widely used as the promoter for the novel low temperature 66
 SCR catalysts. Casapu et al. (2009) compared the effects of 67
 different additives including niobium, iron, tungsten and 68
 zirconium oxide on NH₃-SCR low temperature activity of 69

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MnO_x-CeO_x catalysts and found that the higher activity and superior nitrogen selectivity were obtained by the niobium-doped catalyst. The further investigation indicated that the addition of niobium oxide increased the surface acidity significantly and the interaction between the manganese and niobium led to a good distribution of oxidizing and acidic sites in the catalyst structure (Casapu et al., 2010). Lian et al. (2014b) prepared a series of manganese-niobium mixed oxides catalysts for low temperature NH₃-SCR and concluded that the enhancement of surface acidity by introduction of niobium was responsible for the great low temperature SCR activity. Qu et al. (2013) investigated the relationship between structure and performance of cerium-niobium binary oxide catalysts. The similar conclusion was pointed out that the surface acid sites were mainly provided by niobium oxide species. The novel catalysts such as Nb-promoted CeZr₂O_x catalyst (Ding et al., 2016) and Nb-Ce/WO_x-TiO₂ catalyst (Ma et al., 2012a, b) were also reported in the recent years. Vikulov et al. (1994) found that the promotion effect of niobium for V₂O₅/TiO₂ catalyst was obvious only at low vanadia loadings. However, the specific reason was not explained clearly. Du et al. (2012) reported that either Nb or Sb could improve the SCR activity of V₂O₅/TiO₂ catalyst and co-doping Sb and Nb showed the synergistic effect. Lian et al. (2015b) investigated the promotion effect of Nb addition to VO_x/CeO₂ catalyst and their result showed that 30Nb-1VO_x/CeO₂ exhibited higher NH₃-SCR activity than 3V₂O₅-WO₃/TiO₂.

Even though a lot of researches have been performed, the understanding for the influence of niobium on the SCR activity of V₂O₅-WO₃/TiO₂ is still ambiguous. There was lack of a completed evaluation of the resistance to H₂O and SO₂ for these new catalysts. The SCR activity for them kept decreasing in the presence of SO₂ below 250°C basically (Casapu et al., 2009; Lian et al., 2015b; Ding et al., 2016), which restricted the real application of these novel catalysts. Therefore, we explored the impact of niobium on the 3 wt.% V₂O₅/WO₃-TiO₂ catalyst and performed the systematic evaluation of the resistance to H₂O and SO₂ for the optimized catalyst. Different characterization technologies such as N₂ adsorption-desorption, XRD (X-ray diffraction), NH₃-TPD (temperature programmed desorption), TPSR (temperature programmed surface reaction) and H₂-TPR (temperature programmed reduction) were used to investigate the physical-chemical action of niobium additive. The reason of deactivation in the environment with high concentration SO₂ at low temperatures was clarified by FTIR. The reactivity and decomposition characteristics of ammonium sulfate on catalyst surface were discussed through TPSR and TG-FTIR. Finally, the resistances to H₂O and SO₂ of the particle and monolith catalysts were compared at different temperatures.

1. Experimental

1.1. Catalyst preparation

The Nb doped 3 wt.%V₂O₅/WO₃-TiO₂ catalysts with different contents of niobium oxide (0, 3, 6 and 9 wt.%) were prepared by the wetness impregnation method with the rotary evaporation as the assistance. The commercial WO₃-TiO₂ supporter was purchased from Henan Billions Chemicals Co., Ltd.

(China). Ammonium metavanadate was dissolved in the deionized water with oxalic acid as the promoter. The molar ratio was kept at 1:2 (NH₄VO₃:C₂H₂O₄·2H₂O). Niobium oxalates with different stoichiometric amounts were dissolved in the deionized water, too. Then 20 g WO₃-TiO₂ powder was added into the mixed solution and stirred adequately. The excess water in the mixtures was evaporated in the rotary evaporator at 50°C. Then these samples were dried at 105°C overnight followed by calcination at 500°C in air for 3 hr. The calcined powder samples were pelleted, crushed and sieved to 40–60 mesh for activity evaluation and characterization. The series of catalysts are denoted as 3V_xNb/WTi (x = 0, 3, 6, 9). For comparison, 6 wt.% Nb₂O₅/WO₃-TiO₂ and pure WO₃-TiO₂ supporter were prepared by the same method and labeled as 6Nb/WTi and WTi, respectively.

The (NH₄)₂SO₄-deposited catalyst was prepared using a previously reported wet impregnation method (Zhu et al., 2000; Ye et al., 2016a; Ye et al., 2016b). The loading amount of (NH₄)₂SO₄ was set to 5.0 wt.%. To estimate the function of ammonia during the deactivation process of catalyst in the presence of SO₂, the catalyst was pretreated at 175°C for 3 hr under the condition with 5 vol.% H₂O and 500 ppm SO₂. The corresponding catalyst was denoted as 3V6Nb/WTi-S(175), which meant that 3V6Nb/WTi sample was pretreated with SO₂ at 175°C.

The monolith 3V6Nb/WTi catalyst was prepared by the compression molding method as described in our previous research (Yao et al., 2014). The dried powder sample was mixed with the moderate additives including stearic acid, polyethylene oxide (PEO), carboxymethyl cellulose (CMC), monoethanolamine, activated carbon and deionized water. The monolith catalyst precursor was produced through extrusion and kneading repeatedly. Then the precursor was molded into the monolith shape which was calcined at 500°C for 3 hr to form the final monolith catalyst.

1.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed stainless steel reactor (i.d 10 mm). The total flow rate was 1.5 L/min and the dosage of catalyst was 1.5 mL corresponding to a gas hourly space velocity (GHSV) of 60,000/hr. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH₃, 3.0 vol.% O₂, 5.0 vol.% H₂O (when used), 500 ppm SO₂ (when used) and N₂ as balance gas. The NO, NO₂ and O₂ concentrations were measured by an online flue gas analyzer (NOVA PLUS, MRU, Germany) and the N₂O concentration was monitored by a N₂O IR analyzer (G200, Geotechnical Instruments Ltd., UK). The concentrations of products were recorded after they kept stable for at least 30 min under the test condition. The NO_x conversion was calculated according to the following equation:

$$\text{NO}_x \text{ conversion (\%)} = (1 - [\text{NO}_x]_{\text{out}} / [\text{NO}_x]_{\text{in}}) \times 100\% \quad (1)$$

The (NH₄)₂SO₄ reactivity behavior on the 3V6Nb/WTi catalyst was measured via TPSR with NO. One milliliter catalysts impregnated with (NH₄)₂SO₄ were used for the TPSR test. The samples were passed by the gas containing 400 ppm NO and 3.0 vol.% O₂ at 50°C firstly until the NO concentration in the outlet reached the stable condition. Then

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