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Promotional roles of ZrO_2 and WO_3 in $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-ZrO}_2$ catalysts for NO_x reduction by NH_3 : Catalytic performance, morphology, and reaction mechanism

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ABSTRACT

$\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ catalysts containing various amounts of WO_3 were synthesized. The catalyst morphologies, catalytic performances, and reaction mechanisms in the selective catalytic reduction of NO_x by NH_3 were investigated using in situ diffuse-reflectance infrared Fourier-transform spectroscopy, temperature-programmed reduction (TPR), X-ray diffraction, and the Brunauer-Emmett-Teller (BET) method. The BET surface area of the triple oxides increased with increasing ZrO_2 doping but gradually decreased with increasing WO_3 loading. Addition of sufficient WO_3 helped to stabilize the pore structure and the combination of WO_3 and ZrO_2 improved dispersion of all the metal oxides. The mechanisms of reactions using $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ and $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2$ were compared by using either a single or mixed gas feed and various pretreatments. The results suggest that both reactions followed the Eley-Rideal mechanism; however, the dominant acid sites, which depended on the addition of WO_3 or ZrO_2 , determined the pathways for NO_x reduction, and involved $[\text{NH}_4^+\text{-NO-Brönsted acid site}]^*$ and $[\text{NH}_2\text{-NO-Lewis acid site}]^*$ intermediates, respectively. $\text{NH}_3\text{-TPR}$ and $\text{H}_2\text{-TPR}$ showed that the metal oxides in the catalysts were not reduced by NH_3 and O_2 did not reoxidize the catalyst surfaces but participated in the formation of H_2O and NO_2 .

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1. Introduction

The conventional technique for the control of NO_x emissions is selective catalytic reduction (SCR) of NO_x by NH_3 [1] using various commercial catalysts containing V_2O_5 , WO_3 , and TiO_2 . However, the use of such commercial catalysts is limited because of their low activities (300–400 °C, 85%) [2]. Cheap transition-metal-doped catalysts with exceptional catalytic performances are now widely used in several industrial processes [3]. Previous studies have shown that $\text{TiO}_2\text{-ZrO}_2$ supports have

higher thermal stabilities and amounts of acid sites than pure TiO_2 and ZrO_2 [4]. In this study, we investigated and compared the $\text{NH}_3\text{-SCR}$ mechanisms (above 300 °C) over $\text{V}_2\text{O}_5\text{-x\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ and $\text{V}_2\text{O}_5/9\%\text{WO}_3\text{-TiO}_2$ catalysts.

Although the $\text{NH}_3\text{-SCR}$ mechanism has been widely studied, it is still the subject of much debate. This is because (1) different catalysts have been used, resulting in different active sites and (2) different temperatures have been used in $\text{NH}_3\text{-SCR}$ reactions over different catalysts. Recently, the reactions $\text{NH}_{3(\text{ads})} \rightarrow \text{NO}_{(\text{g})} + \text{O}_{2(\text{g})}$ and $\text{NO}_{(\text{ads})} + \text{O}_{2(\text{ads})} \rightarrow \text{NH}_{3(\text{g})}$ over dif-

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ferent catalysts at different temperatures have been studied and possible reaction pathways have been proposed [5–8]. However, the adsorption behaviors of NH_3 and NO at different temperatures were not clear, e.g., whether and how $\text{NH}_{3(\text{g})}$, $\text{NO}_{(\text{g})}$, and $\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})}$ are adsorbed on the catalyst surface above 300 °C. The differences among the adsorption intensities of these gases are also unclear. Most previous theories have indicated that the reaction involves sequential H abstraction (or oxidation) of NH_3 species to give the coordinated form of NH_3 or the protonated form, i.e., NH_4^+ , followed by partial oxidation by metal oxides (V_2O_5 , WO_3 , and TiO_2) [5–8]. The catalyst surface could therefore be reduced by NH_3 or NH_4^+ . However, temperature-programmed reduction by NH_3 (NH_3 -TPR) of the catalysts has not been investigated, and the proposed catalyst surface reduction by NH_3 is controversial. All these points have important implications for the NH_3 -SCR mechanism, and intensive research to clarify these issues is needed.

In this study, V_2O_5 - WO_3/TiO_2 - ZrO_2 catalysts with various WO_3 loadings were synthesized and used in NH_3 -SCR. The effects of the amounts of WO_3 and ZrO_2 on the catalytic performances and reaction mechanisms over V_2O_5 - WO_3/TiO_2 - ZrO_2 were investigated using the Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), TPR, and in situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS).

2. Experimental

2.1. Catalyst preparation

The V_2O_5 - $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 catalysts were prepared by impregnation of a TiO_2 - ZrO_2 solid solution with ammonium tungstate hydrate and ammonium vanadate.

A TiO_2 - ZrO_2 solid solution (Ti:Zr molar ratio 1:1) was prepared using a precipitation method. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and TiCl_4 (Sinopharm Chemical Reagent) were used as precursors. Ammonia water (25%–28%) was added dropwise to the metal precursor solution at 25 °C until the pH was between 9 and 10. The obtained milky slurry was aged in the solution at 25 °C for 24 h. The hydroxide was filtered off, washed with deionized water, and dried at 110 °C for 12 h. The samples were calcined at 450 °C in air for 3 h before milling and screening to 60 mesh.

An incipient wetness impregnation method was used to synthesize $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 ($x = 0, 6, 9, 12$, weight ratio). $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot x\text{H}_2\text{O}$ (Sinopharm Chemical Reagent) was added to the TiO_2 - ZrO_2 carrier and the mixture was stirred at 35 °C for 2 h. The residue obtained by evaporation at 80 °C was dried at 110 °C for 12 h. The samples were calcined at 450 °C in air for 3 h, and milled and screened to 60 mesh. The same procedure was used to synthesize $9\%\text{WO}_3/\text{TiO}_2$ with anatase TiO_2 as the carrier.

A wet impregnation method was used to synthesize $1\%\text{V}_2\text{O}_5$ - $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 and $1\%\text{V}_2\text{O}_5$ - $9\%\text{WO}_3/\text{TiO}_2$ as follows. NH_4VO_3 (Sinopharm Chemical Reagents) was added to $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 powder and $9\%\text{WO}_3/\text{TiO}_2$ powder; the rest of the process was the same as that used to prepare $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 .

We denote $1\%\text{V}_2\text{O}_5$ - $x\%\text{WO}_3/\text{TiO}_2$ - ZrO_2 by $x\%\text{WO}_3$, where x represents the amount of WO_3 in the catalyst.

2.2. Catalyst characterization

XRD patterns of the catalysts were obtained using an XD-3 diffractometer (Beijing PEPSEE, China) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The specific surface areas of the catalysts were measured based on N_2 adsorption-desorption at liquid N_2 temperature (−196 °C) using a Micromeritics F-sorb 3400 adsorption apparatus (Beijing Jinaipu, China). NH_3 -TPR was performed in a quartz U-tube reactor connected to a thermal conductivity detector, using an NH_3 -He mixture (0.503 vol% NH_3) as a probe. TPR was performed from 25 to 700 °C at a rate of 10 °C/min.

In situ (DRIFTS) was performed using a Nicolet 6700 FT-IR instrument (Thermo Electron Corporation, USA) with a Harrick accessory (HTC-3, Harrick Scientific Corporation, USA) in the wavenumber range 400–4000 cm^{-1} at a 4 cm^{-1} resolution. NH_3 -adsorbed in situ DRIFTS was performed as follows. (1) A thin, intact, self-supporting wafer of the catalyst (10 mg) was prepared and mounted inside a high-temperature cell (HTC-3, Harrick Scientific Corporation, USA) and subjected to a high-purity N_2 stream at 400 °C for 1 h. (2) After cooling to room temperature, the wafer was exposed to an NH_3 (99.999%) stream at a flow rate of 5 mL/min for 30 min. (3) The wafer was flushed with a high-purity N_2 stream for 30 min. (4) IR spectra were recorded at various target temperatures in a high-purity N_2 stream; the temperature was increased at a rate of 10 °C/min.

2.3. Catalyst activity test

The catalytic activity was investigated in a fixed-bed stainless-steel reactor (i.d. 6 mm) at 200–450 °C, using 300 mg of catalyst. A gas mixture of 0.08% NO , 0.08% NH_3 , and 5% O_2 (by volume) was fed into the reactor and N_2 was used to give a total flow rate of 100 mL/min (gas hourly space velocity (GHSV) = 20000 h^{-1}). The NO and NO_2 concentrations were continually monitored using a flue gas analyzer (Testo 350-XL).

3. Results and discussion

3.1. Specific surface area and pore size

The specific surface areas and pore size distributions of the catalysts are shown in Table 1 and Fig. 1. The pore size distributions clearly show that the amounts of pores of sizes 384.2–8.3 nm and 3.1–1.7 nm were unchanged by WO_3 addition, but the amounts of pores of size 8.3–3.9 nm increased greatly. This indicates that WO_3 addition enhanced the thermal stability of the pore structure, especially of pores of size 8.3–3.9 nm. The BET surface areas (S_{BET}) decreased with increasing WO_3 loading. The XRD patterns (Fig. 2) show that no crystalline tungsten oxide was present on the catalyst surfaces. This suggests that amorphous WO_3 was dispersed on the surface of the TiO_2 - ZrO_2 support and occupied the pores, decreasing the sur-

Table 1

BET surface area of different catalysts.

Sample	S_{BET} (m ² /g)
V ₂ O ₅ /TiO ₂ -ZrO ₂	143.77
V ₂ O ₅ -6%WO ₃ /TiO ₂ -ZrO ₂	199.60
V ₂ O ₅ -9%WO ₃ /TiO ₂	60.86
V ₂ O ₅ -9%WO ₃ /TiO ₂ -ZrO ₂	197.57
V ₂ O ₅ -12%WO ₃ /TiO ₂ -ZrO ₂	181.85

face area. WO₃ addition increased the BET surface area of V₂O₅/TiO₂-ZrO₂. This suggests that WO₃ acts as a structural promoter by improving the structural properties of the catalysts [9,10]. The BET surface area of the four-component catalyst obtained by ZrO₂ addition was considerably higher than that of the triple-oxide catalyst. This is because of the high surface area of the TiO₂-ZrO₂ solid-solution support. However, the results of experiments using the V₂O₅/TiO₂-ZrO₂ and V₂O₅-9%WO₃/TiO₂ catalysts suggest that the surface area may not determine the catalytic performance.

3.2. Crystalline phase analysis

The XRD patterns of the catalysts are shown in Fig. 2. The tetragonal phase of vanadium oxide was identified in the V₂O₅/TiO₂-ZrO₂ catalyst; the peak at 27.5° was ascribed to rutile TiO₂ and those at 25.3° and 53.97° were ascribed to anatase TiO₂ [11]. Sharp peaks ascribable to zirconium oxide were

Fig. 2. XRD patterns of different samples. (1) V₂O₅/TiO₂-ZrO₂; (2) V₂O₅-6%WO₃/TiO₂-ZrO₂; (3) V₂O₅-9%WO₃/TiO₂-ZrO₂; (4) V₂O₅-12%WO₃/TiO₂-ZrO₂; (5) V₂O₅-9%WO₃/TiO₂.

clearly observed. The V₂O₅-x%WO₃/TiO₂-ZrO₂ catalysts had similar XRD patterns; no crystalline-phase peaks were observed, suggesting that these metal oxides did not form large crystals, indicating that addition of WO₃ improved dispersion of metal oxides on the support. A comparison of the XRD pattern of 9%WO₃ with that of the V₂O₅-9%WO₃/TiO₂ catalyst suggests that ZrO₂ doping facilitated dispersion of all metal oxides, with no crystalline peaks being observed for titanium oxide (anatase or rutile). These results show that addition of WO₃ and ZrO₂ gave well-dispersed four-component catalysts.

3.3. In situ DRIFTS analysis

The surface acidities of the catalysts were investigated using in situ DRIFTS analysis of NH₃ adsorption. The bands at 1155–1222 and 1600–1624 cm⁻¹ in the spectra can be assigned to symmetric and asymmetric vibrations, respectively, of the N–H bonds in NH₃ coordinated to Lewis acid sites [12,13]. The bands at 1450 and 1680 cm⁻¹ correspond to the asymmetric and symmetric vibrations, respectively, of NH₄⁺ ions formed by NH₃ chemisorption at Brønsted acid sites [14]. All the samples were exposed to NH₃ (10 mL/min), followed by N₂ purging at 25 to 400 °C.

For the V₂O₅/TiO₂-ZrO₂ catalyst (Fig. 3(a)), bands appeared at 1180, 1450, and 1680 cm⁻¹ after N₂ purging; this implies that the catalyst has both Brønsted and Lewis acid sites. The bands at 1450 and 1680 cm⁻¹ completely disappeared at 200 °C, but the band at 1180 cm⁻¹ was still present at 400 °C. This suggests that the NH₄⁺-Brønsted acid species was not very stable [15].

For the WO₃-modified counterpart (Fig. 3(b)–(d)), the band at 1450 cm⁻¹ did not vanish until the temperature was 250 °C, suggesting that WO₃ addition improved the stability of the Brønsted acid species [14]. Fig. 4 shows that the intensity of the peak at 1180 cm⁻¹ was not affected by the amount of WO₃ added, but the intensity of the band at 1454 cm⁻¹ was: V₂O₅-9%WO₃/TiO₂-ZrO₂ > V₂O₅-12%WO₃/TiO₂-ZrO₂ > V₂O₅-6%WO₃/TiO₂-ZrO₂ > V₂O₅/TiO₂-ZrO₂. This implies that WO₃ addition increases the number of Brønsted acid sites.

Fig. 3 shows that at 250 °C the amount of NH₄⁺ (1450 cm⁻¹)

Fig. 1. Pore size distributions of various catalysts.

Fig. 3. In situ DRIFT spectra of NH_3 adsorption at various temperatures over (a) $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$, (b) $\text{V}_2\text{O}_5\text{-6\%WO}_3/\text{TiO}_2\text{-ZrO}_2$, (c) $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$, and (d) $\text{V}_2\text{O}_5\text{-12\%WO}_3/\text{TiO}_2\text{-ZrO}_2$.

decreased significantly at 250 °C, but coordinated NH_3 could still be observed above 250 °C. The residence time of coordinated NH_3 was therefore longer than that of adsorbed NH_4^+ . NO_x reduction is a surface reaction, therefore a longer residence time benefits NO_x reduction. For the $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ sample (Fig. 4), the intensity of the Lewis acid peak was weaker than that for $\text{V}_2\text{O}_5\text{-12\%WO}_3/\text{TiO}_2\text{-ZrO}_2$, but the intensity of the Brønsted acid peak was much stronger. The large number of Brønsted

acid sites enabled reduction of a large amount of NH_4^+ in a short residence time (Fig. 6(a)). This is one of the reasons why NO_x conversion over $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ was higher than that over $\text{V}_2\text{O}_5\text{-12\%WO}_3/\text{TiO}_2\text{-ZrO}_2$.

Fig. 5 shows that a weak band appeared at 1550 cm^{-1} after NH_3 adsorption on the $\text{V}_2\text{O}_5\text{-x\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ samples. Similar bands from intermediate species have previously been detected over vanadium-based catalysts after reaction with NH_3 , and were assigned to $-\text{NH}_2$ amide species [12,16]. This result confirms that WO_3 addition promoted NH_3 activation.

3.4. Catalytic performances

Fig. 6(a) shows the SCR activities of the $\text{V}_2\text{O}_5\text{-x\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ catalysts. The highest NO_x conversion was achieved over $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ between 300 and 450 °C. The reasons might be as follows. (1) It had a large number of Brønsted acid sites (Fig. 4); (2) the pores of size 8.3–3.9 nm (mesopores: 50–2 nm) were stable (Fig. 1); (3) the good dispersion obtained by addition of 9% WO_3 increased strong interactions among the metal oxides (Fig. 2). Although the BET surface area of $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ was much higher than that of $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2$, the catalytic performance of the latter sample was better in the required temperature window, implying that the surface area was not the major factor in the

Fig. 4. In situ DRIFT spectra of different catalysts recorded at 100 °C.

Fig. 5. In situ DRIFT spectra of NH_3 desorption at 100 °C over (a) $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$, (b) $\text{V}_2\text{O}_5\text{-6\%WO}_3/\text{TiO}_2\text{-ZrO}_2$, (c) $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$, and (d) $\text{V}_2\text{O}_5\text{-12\%WO}_3/\text{TiO}_2\text{-ZrO}_2$.

Fig. 6. NO_x conversions of over different catalysts with (a) and without (b) O_2 .

catalytic performance. It can be concluded that a combination of the above-mentioned properties of the $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$ sample was the main reason for its higher catalytic performance.

Fig. 6(b) shows that without O_2 (at the same GHSV), NO_x conversion decreased greatly, indicating that the presence of O_2 accelerates NO_x conversion. The role of O_2 will be discussed in detail in Section 3.6.

The effects of SO_2 and H_2O on NO_x reduction were also studied, using 6% H_2O and various amounts of SO_2 in the gas mixture at the same GHSV. Fig. 7 shows that NO_x conversion decreased significantly in the presence of H_2O and SO_2 . When the H_2O and SO_2 feeds were stopped, the catalytic activity was not completely recovered, which implies that H_2O and SO_2 poisoning of the catalysts was partly irreversible. The poisoning effect was more apparent with increasing SO_2 concentration.

3.5. $\text{NH}_3\text{-SCR}$ mechanism

3.5.1. NH_3 , NO , and $\text{NO} + \text{O}_2$ adsorption

Fig. 7. Effects of H_2O and SO_2 on SCR catalytic activity of $\text{V}_2\text{O}_5\text{-9\%WO}_3/\text{TiO}_2\text{-ZrO}_2$.

Fig. 8. In situ DRIFT spectra of V_2O_5 - $x\%$ WO_3 / TiO_2 - ZrO_2 exposed to NH_3/N_2 (a) and NO/N_2 (b) at 300 °C for 30 min and 5 mL/min.

Fig. 9. In situ DRIFT spectra of V_2O_5 - $x\%$ WO_3 / TiO_2 - ZrO_2 exposed to NH_3/N_2 (a) and NO/N_2 (b) at 350 °C and 5 mL/min for 30 min.

The adsorption properties of the SCR reactants over V_2O_5 - $x\%$ WO_3 / TiO_2 - ZrO_2 catalysts were investigated extensively. Figs. 8(a) and 9(a) show DRIFT spectra of the catalysts after exposure to NH_3/N_2 at for 30 min at 300 and 350 °C. The bands at 1610, 1214, and 1321 cm^{-1} are attributed to asymmetric and symmetric deformation, respectively, of NH_3 coordinated with Lewis acid sites and adsorbed NH_3 gas. Coordinated NH_3 is clearly the dominant species during NH_3 adsorption. Figs. 8(b) and 9(b) show that a weak band appeared at 1621 cm^{-1} ($\nu_{as}(NO_2)$), indicating that SCR involved gaseous NO or weakly adsorbed NO_2 ; these results are consistent with those previously reported [17,18].

The IR spectra of NO + O_2 co-adsorbed at 300 °C are shown in Fig. 10. After introduction of NO + O_2 into the cell for 30 min, the same band appeared at 1621 cm^{-1} , assigned to $\nu_{as}(NO_2)$ [19–22]; the intensity of the NO band was the same regardless of whether or not O_2 was introduced. NO and O_2 readily react to produce NO_2 , but NO_2 is not easily adsorbed on the catalyst surface. A comparison of the adsorption states and intensities of NH_3 and NO showed the following. (1) Above 300 °C, NH_3 -SCR involved strongly adsorbed NH_3 and gaseous or weak NO_2 species, and NO could only be adsorbed onto the catalyst surface as NO_2 . (2) Above 300 °C, the catalytic reaction over V_2O_5 - $x\%$ WO_3 / TiO_2 - ZrO_2 could only follow the Eley-Rideal

mechanism (the catalytic reaction occurred between adsorbed molecules A and B; molecule B was weakly adsorbed or not adsorbed). (3) For the V_2O_5 - $x\%$ WO_3 / TiO_2 - ZrO_2 samples, it can be concluded that the catalyst activated NH_3 and could not activate NO. This conclusion is supported by the suggestion that NO reacts in the gas phase and is almost unable to be adsorbed and then activate NO.

Fig. 10. IR spectra after exposure of V_2O_5 -9% WO_3 / TiO_2 - ZrO_2 catalyst to NO (5 mL/min) + O_2 (10 mL/min).

3.5.2. Reaction between $\text{NH}_3(\text{ads})$ and $\text{NO}(\text{g}) + \text{O}_2(\text{g})$ over $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$

The $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ catalysts had similar adsorption properties, therefore $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ was selected to study the $\text{NH}_3\text{-SCR}$ mechanism in-depth because it gave the highest NO_x conversion. The investigation was performed at 300 °C using $\text{NO} + \text{O}_2$ as the reactants. Figs. 11 and 12 show the in situ DRIFT spectra over $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ pretreated by exposure to NH_3/N_2 (5 mL/min), followed by NO (5 mL/min) + O_2 (10 mL/min) at 300 °C. During NH_3 adsorption and N_2 purging (Figs. 11(a) and 12(a)), bands were detected at 1204, 1550, 1602, 3156, 3264, and 3347 cm^{-1} . The band at 1550 cm^{-1} was ascribed to the -NH_2 scissoring mode of an inorganic amide species, and those at 1602, and 1204 and 3347 cm^{-1} were ascribed to asymmetric and symmetric deformations, respectively, of coordinated NH_3 . The bands at 3156 and 3264 cm^{-1} were ascribed to the overtone of the asymmetric NH_3 deformation as a result of Fermi resonance [23]. It is worth noting that all the bands remained during N_2 purging. These results show that Lewis acid sites were the active acid sites above 300 °C. When the NH_3 -loaded catalyst was exposed to $\text{NO} + \text{O}_2$ (Figs. 11(b) and 12(b)), all the band intensities decreased continuously in the period from 30 to 50 min, possibly

because $\text{NO}(\text{g})$ reacted with the $\text{-NH}_2(\text{ads})$ [24] to form the intermediate $[\text{NH}_2\text{-NO}]$; this activated complex then decomposed to yield N_2 and H_2O . During the $\text{NO} + \text{O}_2$ reaction, a new band appeared at 1595 cm^{-1} , ascribed to the bending vibration of H_2O [25]. When $\text{NO} + \text{O}_2$ was introduced onto the NH_3 -loaded catalyst for 30 min (Fig. 12(c)), a new peak emerged at 3657 cm^{-1} (symmetric deformation of H_2O). These results prove that H_2O was formed during the $\text{NO} + \text{O}_2$ reaction.

3.5.3. Reaction between $\text{NH}_3(\text{ads})$ and $\text{NO}(\text{g}) + \text{O}_2(\text{g})$ over $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2$

Figs. 13 and 14(a) show in situ DRIFT spectra of the $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2$ catalysts exposed to NO (Fig. 13(a)), $\text{NO} + \text{O}_2$ (Fig. 13(b)), and NH_3 (Fig. 14(a)) at 300 °C. Fig. 13 shows two bands at 1365 and 1621 cm^{-1} , which were assigned to the symmetric and asymmetric deformations, respectively, of NO_2 [25]; the intensities of these two bands were close to zero regardless of whether or not O_2 was introduced. The bands at 1248, 1325, 1437, and 1668 cm^{-1} in Fig. 14(a) were ascribed to the symmetric stretching vibrations of NH_3 , gas-adsorbed NH_3 , and symmetric and asymmetric deformations of NH_4^+ [18]. The following conclusions can be drawn from Figs. 13 and 14(a). (1) NO can only be adsorbed on the surface in the form of NO_2 . (2)

Fig. 11. In situ DRIFT spectra of $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ exposed to NH_3/N_2 (a) followed by exposure to $\text{NO} + \text{O}_2$ (b).

Fig. 12. In situ DRIFT spectra of $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ exposed to NH_3/N_2 (a) followed by exposure to $\text{NO} + \text{O}_2$ (b). (c) In situ DRIFT spectra of NH_3 -adsorbed catalysts with $\text{NO} + \text{O}_2$ purging for 50 min: red, H_2O formation; blue, NH_3 consumption.

Fig. 13. In situ DRIFT spectra of V_2O_5 -9% WO_3 / TiO_2 exposed to (a) NO and NO + O_2 (b) at 300 °C.

Fig. 14. In situ DRIFT spectra of V_2O_5 -9% WO_3 / TiO_2 catalyst: (a) exposed to NH_3 (5 mL/min) and then (b) NO (5 mL/min) + O_2 (10 mL/min); (c) formation of H_2O over V_2O_5 -9% WO_3 / TiO_2 at 300 °C.

Adsorbed NH_4^+ and coordinated NH_3 were the dominant species during NH_3 adsorption and both of them were stronger adsorbates than NO; these results are consistent with those of research on vanadia-based catalysts [17]. (3) Brönsted and Lewis acid sites were the active sites on the V_2O_5 -9% WO_3 / TiO_2 catalyst above 300 °C. (4) The Brönsted acid sites were not always weaker than the Lewis acid sites. Ramis reported that NH_4^+ adsorbed on Brönsted acid sites was less thermally stable than coordinated NH_3 , indicating less involvement of NH_4^+ in SCR under the conditions used [5]. The adsorption states of NH_3 and NO suggest that the catalytic reaction followed the Eley-Rideal mechanism in the case of V_2O_5 -9% WO_3 / TiO_2 .

In situ DRIFT spectra of the V_2O_5 -9% WO_3 / TiO_2 catalyst after adsorption of NH_3 and then flushing with NO + O_2 are shown in Fig. 14(b). During NO + O_2 purging, the bands at 1260 ($\delta_s(\text{NH}_3)$), 1302 (adsorbed NH_3 gas), 1440 ($\delta_{\text{as}}(\text{NH}_4^+)$), 1680 ($\delta_s(\text{NH}_4^+)$), 3152 and 3264 ($\gamma(\text{NH}_3)$), and 3347 ($\gamma_s(\text{NH}_3)$) continually decreased as NO + O_2 was fed to the NH_3 -saturated catalyst. Fig. 15 (e) (partial enlarged drawing) shows that the band at 1543 ($-\text{NH}_2$) also disappeared gradually as NO + O_2 was introduced into the NH_3 -saturated catalyst. The pathway of NO_x removal might therefore be as follows: $\text{NH}_4^+(\text{ads})$ reacts with $\text{NO}_{(\text{g})}$, $\text{NH}_2(\text{ads})$ reacts with $\text{NO}_{(\text{g})}$ and then the complexes

$[\text{NH}_4^+-\text{NO}]$ and $[\text{NH}_2-\text{NO}]$ decompose to N_2 and H_2O .

After feeding a gas mixture of NO and O_2 , all the above bands vanished (Fig. 14(b)), which clearly shows that NH_3 can reduce NO all the way from $\text{NO}_{(\text{g})}$ to N_2 . Two new bands, at 3657 and 3733 cm^{-1} , appeared simultaneously after purging with NO + O_2 for 30 min (Fig. 14(c)); these provide good evidence of the formation of adsorbed H_2O [26,27].

3.6. Role of O_2

IR spectra of V_2O_5 -9% WO_3 / TiO_2 - ZrO_2 and V_2O_5 -9% WO_3 / TiO_2 were recorded to enable further understanding of the role of O_2 in SCR. The samples were pretreated with NH_3 (5 mL/min) at 300 °C, followed by NO (5 mL/min) and N_2 (10 mL/min). Fig. 15 shows that intensities of the bands at 1260 ($\delta_s(\text{NH}_3)$), 1450 ($\delta_{\text{as}}(\text{NH}_4^+)$), and 1542 ($\gamma(\text{NH}_2)$) cm^{-1} (Fig. 16(a)), 3156 and 3264 ($\gamma(\text{NH}_3)$), and 3347 ($\gamma_s(\text{NH}_3)$) cm^{-1} (Fig. 15(a) and (b)) decreased slowly with NO feeding. The band at 3600–3800 cm^{-1} (OH groups) was not observed after purging with NO (Fig. 16(b)). For V_2O_5 -9% WO_3 / TiO_2 - ZrO_2 (Fig. 15(c) and (d)), similar phenomena were observed, i.e. the bands at 1204, 1542 (Fig. 16(c)), 3167, 3264, and 3347 cm^{-1} slowly shrank when NO was introduced. The band at around

Fig. 15. In situ DRIFT spectra at 300 °C. (a) exposure to NH₃ and then (b) NO for V₂O₅-9%WO₃/TiO₂; (c) exposure to NH₃ and then (d) NO for V₂O₅-9%WO₃/TiO₂-ZrO₂. (e) In situ DRIFT spectra of NH₃-adsorbed V₂O₅-9%WO₃/TiO₂ exposed to NO at 300 °C (partial enlarged drawing): (1) NH₃ adsorption for 80 min; (2) N₂-purging for 30 min; (3–6) NO + O₂ exposure for various times.

3370 cm⁻¹, corresponding to H₂O, did not appear (Fig. 16(d)).

Fig. 6(b) shows that the NO_x conversions over V₂O₅-9%WO₃/TiO₂-ZrO₂ and V₂O₅-9%WO₃/TiO₂ decreased significantly when O₂ was not present; this suggests that gaseous O₂ was crucial in the formation of H₂O. Fig. 17 also shows that NO was easily oxidized by O₂. Most researchers proposed [14,28,29] that the reaction of NH₃ with NO, resulting in partial reduction of O₂, can be explained by the need for the surface to be reoxidized by gaseous O₂ to complete the catalytic cycle. We used NH₃-TPR and H₂-TPR to confirm this. In the H₂-TPR profiles in Fig. 18, the peak at 385 °C was assigned to V₂O₅ → V₂O₃ [30], the peak at 697 °C was assigned to V₃O₁₃ → V₂O₄, the peak at 545 °C was assigned to TiO₂ → Ti_xO_y, and the peak at 750 °C was assigned to WO_{2.9} → W. These results show that the catalyst could be reduced by H₂. However, the NH₃-TPR results suggested otherwise. A new peak appeared at 575 °C, indicating that a new gas (with a different thermal conductivity coefficient) was formed, as a result of the design of the TPR instrument; above 575 °C, the electrical signal suddenly changed significantly. It is possible that NH₃ decomposed to N₂ and other gases above 500 °C. The NH₃-TPR results show that the metal oxides in the catalyst were not reduced by NH₃. The original hypothesis that the catalyst surface would be reoxidized by O₂ to complete the catalytic cycle is incorrect, and gaseous O₂

merely takes part in the formation of H₂O and NO₂.

3.7. Possible pathway (NO_x removal)

Most research clearly supports the Brönsted-NH₄⁺ mechanism. This mechanism was proposed by Topsøe [14,31,32], who suggested that adsorbed NH₃ was activated by transfer of an H atom to V⁵⁺=O, leading to reduction of gaseous or weakly adsorbed NO, with subsequent reaction with the activated NH₃, to yield N₂ and H₂O with release of V⁵⁺-OH and V⁴⁺-OH; the cycle was completed by oxidation of V⁴⁺-OH to V⁵⁺=O. Another mechanism (the Lewis acid mechanism) was proposed by Ramis et al. [33] and supported by Bagnasco et al. [34]. This mechanism also involves the transformation of Mⁿ⁺ to M⁽ⁿ⁻¹⁾⁺. The same conclusion was reached, i.e., that the catalyst was reduced by NH₃. However, the NH₃-TPR results show that the catalyst was not reduced by NH₃ during NH₃-SCR (V₂O₅-9%WO₃/TiO₂ and V₂O₅-9%WO₃/TiO₂-ZrO₂ gave similar NH₃-TPR results). The traditional mechanism is therefore not supported. V₂O₅ was the main active ingredient during NH₃-SCR; the NO_x conversions over TiO₂-ZrO₂ and V₂O₅/TiO₂-ZrO₂ provide the best proof (Fig. 19); WO₃ improved the stability of the catalyst structure (Fig. 1). The NO_x removal pathways via Lewis and Brönsted acid sites are shown in

Fig. 16. In situ DRIFT spectra of NH_3 -adsorbed catalysts: after (a) N_2 purging and then (b) NO purging at 300°C for V_2O_5 -9% WO_3/TiO_2 ; (c) N_2 purging and then (d) NO purging at 300°C for V_2O_5 -9% WO_3/TiO_2 - ZrO_2 .

Fig. 20.

The pathways can be explained as follows. For Lewis acid sites, $\text{NH}_3(\text{g})$ is adsorbed on the catalyst surface in the form of a coordination compound. When the unshared electron pair enters the $3d$ orbital of V , the N-H bond is broken because of the strong electronegativity of the O atom ($3.44 > \text{N } 3.04$) and then intermediate **3** appears. Lastly, when gaseous NO is fed to the NH_3 -adsorbed catalyst, the intermediate $[\text{NH}_2\text{-NO}]^*$ decomposes to N_2 and H_2O . For the Brönsted acid sites, the ad-

Fig. 17. Concentrations of reactant gases in SCR over V_2O_5 -9% WO_3/TiO_2 - ZrO_2 at 300°C .

sorbed NH_3 generates NH_4^+ , which reacts with $\text{NO}(\text{gas})$ to form the intermediate $[\text{NH}_4^+\text{-NO}]^*$. Finally, this activated complex decomposes via $[\text{NH}_4^+\text{-NO}]$, presumably to N_2 and H_2O . During NH_3 -SCR, the catalyst is not reduced by NH_3 , unlike the traditional NH_3 -SCR pathway.

4. Conclusions

Addition of sufficient WO_3 stabilized the pore structure and a combination of WO_3 and ZrO_2 improved dispersion of all the metal oxides. In particular, addition of 9% WO_3 addition significantly increased the amount of Brönsted acid sites and improved the thermally stability of the pore structure (3.9–8.3 nm); this contributed to the higher NO_x conversion over V_2O_5 -9% WO_3/TiO_2 - ZrO_2 . ZrO_2 doping considerably increased the BET surface area of the triple-oxide catalyst (V_2O_5 -9% WO_3/TiO_2) and improved dispersion of the active components on the surface. However, its main promotional role was to change the surface acidity of V_2O_5 - WO_3/TiO_2 . The pathway of NO_x reduction changed accordingly. There are only Lewis acid sites on the catalyst supported on TiO_2 - ZrO_2 , but there are both Brönsted and Lewis acid sites on the catalyst supported on TiO_2 . The adsorption properties of NO (gaseous or weakly adsorbed) and NH_3 (strongly adsorbed) determine the catalytic mechanism. The catalysts studied follow the

Fig. 18. NH₃-TPR and H₂-TPR profiles over V₂O₅-9%WO₃/TiO₂ (a) and V₂O₅-9%WO₃/TiO₂-ZrO₂ (b).

Eley-Rideal mechanism, but different dominant acid sites lead to different pathways for NO_x reduction, i.e., via [NH₄⁺-NO-Brønsted acid site]* intermediates for V₂O₅-x%WO₃/TiO₂-ZrO₂ and via [NH₂-NO-Lewis acid site]* intermediates for V₂O₅-9%WO₃/TiO₂. The metal oxides in the catalyst are not reduced by NH₃ and O₂ cannot reoxidize the catalyst surface, but participates in the formation of H₂O and NO₂.

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Fig. 19. NO_x conversions by two catalysts.

Fig. 20. Pathways for NO_x removal for different acid sites.

Graphical Abstract

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Promotional roles of ZrO₂ and WO₃ in V₂O₅-WO₃/TiO₂-ZrO₂ catalysts for NO_x reduction by NH₃: Catalytic performance, morphology, and reaction mechanismYaping Zhang, Longfei Wang, Juan Li, Huiyan Zhang*, Haitao Xu, Rui Xiao, linjun Yang
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WO₃ and ZrO₂ facilitated dispersion of all metal oxides on catalysts. The addition of WO₃ or ZrO₂ led to different pathways for NO_x reduction, involving either [NH₄⁺-NO-Brønsted acid site]* and [NH₂-NO-Lewis acid site]* intermediates.

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V₂O₅-WO₃/TiO₂-ZrO₂ 脱硝催化剂中 ZrO₂ 和 WO₃ 的促进作用：催化性能、形态及反应机理

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摘要: 商业选择性催化还原 (SCR) 催化剂成分主要有 V₂O₅, WO₃ 和 TiO₂, 但适用温度窗口较窄 (300–400 °C), 使得实际操作过程中活性较低。目前, 过渡金属广泛应用于催化剂制备中以提高其催化活性。相比于纯 TiO₂ 和 ZrO₂ 载体, TiO₂-ZrO₂ 具有较高的热稳定性以及较多的酸位, 虽然有关 TiO₂-ZrO₂ 为载体的催化剂研究较多, 但未与商业催化剂进行对比研究。而针对 NH₃-SCR 脱硝机理的实验研究也存在一些争议, 主要原因归为以下两方面: (1) 多数催化剂不同会直接导致催化剂的活性酸位不同; (2) 不同 NH₃-SCR 脱硝催化剂的起活温度不同。同时, NH₃ 和 NO 在反应温度的吸附情况仍需要进一步研究。因此, 有必要深入探究 NH₃-SCR 脱硝机理, 以解决现行研究中存在的问题。

本文首先采用共沉淀法制备摩尔比为 1:1 的 TiO₂-ZrO₂ 固溶体, 并分步浸渍不同质量比的 WO₃ 和 1%V₂O₅, 最终得到一系列 1%V₂O₅-x%WO₃/TiO₂-ZrO₂。然后通过 X 射线衍射 (XRD) 和比表面积测试 (BET)、程序升温还原 (TPR)、原位漫反

射红外光谱 (in situ DRIFTS) 研究了 WO_3 和 ZrO_2 对催化性能的影响以及 $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂的反应机理。

N_2 物理吸附结果表明, WO_3 的添加使得催化剂孔结构的热稳定性有所提高, 同时随着 WO_3 含量增加催化剂的比表面积逐渐减小, 但仍高于 $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ 催化剂; ZrO_2 对催化剂比表面积增大效果比较明显。结合 XRD 结果表明, WO_3 能促进金属氧化物在载体上的分散; 相比于 $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 催化剂, ZrO_2 有利于活性组分的分散负载。

比较系列 $\text{V}_2\text{O}_5\text{-}x\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 的氨吸附情况, 发现 WO_3 的添加增加了 Brönsted 酸的稳定性, 其中以 9% WO_3 的效果最显著。催化剂氨吸附中间物种 ($-\text{NH}_2$) 的发现, 证实了 WO_3 添加促进了 NH_3 的活化, 有利于脱硝反应的进行。

SCR 反应结果显示, $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂在 300–450 °C 时 NO_x 转化效率最优, 并发现 O_2 的存在促进了 NO_x 的转化。

采用 in situ DRIFTS 研究了 $\text{V}_2\text{O}_5\text{-}x\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂脱硝机理, 300 和 350 °C 时 NH_3 , NO , $\text{NO} + \text{O}_2$ 吸附情况表明, 在真实的反应温度下, 脱硝过程中的活性中心为 Lewis 酸中心, Brönsted 酸中心的 NH_4^+ 极易从催化剂表面脱附, 无法吸附在催化剂表面, 且与 NH_3 相比, NO 只能以 NO_2 的形式弱吸附在催化剂表面。因此, 该催化剂遵循 Eley-Rideal 脱硝机理。而 $\text{V}_2\text{O}_5\text{-}9\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂具有相对较高的脱硝效率, 因此用来着重研究 $\text{NH}_3\text{-SCR}$ 机理。在 NH_3 吸附过程中, NH_3 (1204, 1602, 3156, 3264, 3347 cm^{-1}) 和活性中产物 NH_2 (1550 cm^{-1}) 在催化剂表面的吸附 (恒温 300 °C) 是稳定的; 随后通入 $\text{NO} + \text{O}_2$ 时, NH_3 吸附过程中的所有吸收峰 (包括 NH_2) 均逐渐减小 (NH_3 吸附态与 NO 结合后分解为 N_2 和 H_2O), 同时出现 H_2O 的振动峰, 这证明了 $\text{V}_2\text{O}_5\text{-}x\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂的脱硝反应过程。

各类气体吸附情况表明, NO 在商业催化剂的吸附状态与 $\text{V}_2\text{O}_5\text{-}x\%\text{WO}_3/\text{TiO}_2\text{-ZrO}_2$ 催化剂相同; 但 NH_3 吸附结果表明, Brönsted 酸中心和 Lewis 酸中心都是催化剂的活性中心; $\text{NO} + \text{O}_2$ 的通入使得催化剂表面的 NH_3 和 NH_4^+ 都逐渐消失。这两种催化剂脱硝反应过程差异主要在于催化剂表面活性中心的不同, 导致了不同的 NO_x 脱除路径。

通过 in situ DRIFTS 比较 O_2 的存在对脱硝反应产生的不同影响来确定 O_2 的作用。两类催化剂上 O_2 均参与了 H_2O 的形成, 促进了催化反应的完成; 当 O_2 不存在时, NO 的还原受到了极大地抑制, 同时也未出现 H_2O ; 两者的脱硝效率大大降低。 $\text{H}_2\text{-TPR}$ 和 $\text{NH}_3\text{-TPR}$ 结果进一步证实 O_2 的作用主要是氧化 NO 及参与催化过程 H_2O 的形成。

关键词: 二氧化钨; 三氧化钨; 氨气选择性催化还原; 原位漫反射红外; 反应机理

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