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In Situ DRIFTS Studies of NH_3-SCR Mechanism over V_2O_5-CeO_2/TiO_2-ZrO_2 Catalysts for Selective Catalytic Reduction of NO_x

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Abstract: TiO_2-ZrO_2 (Ti-Zr) carrier was prepared by a co-precipitation method and 1 wt. % V_2O_5 and 0.2 CeO_2 (the Mole ratio of Ce to Ti-Zr) was impregnated to obtain the V_2O_5-CeO_2/TiO_2-ZrO_2 catalyst for the selective catalytic reduction of NO_x by NH_3. The transient activity tests and the in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) analyses were employed to explore the NH_3-SCR (selective catalytic reduction) mechanism systematically, and by designing various conditions of single or mixing feeding gas and pre-treatment ways, a possible pathway of NO_x reduction was proposed. It was found that NH_3 exhibited a competitive advantage over NO in its adsorption on the catalyst surface, and could form an active intermediate substance of -NH_2. More acid sites and intermediate reaction species (-NH_2), at lower temperatures, significantly promoted the SCR activity of the V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst. The presence of O_2 could promote the conversion of NO to NO_2, while NO_2 was easier to reduce. The co-existence of NH_3 and O_2 resulted in the NH_3 adsorption strength being lower, as compared to tests without O_2, since O_2 could occupy a part of the active site. Due to CeO_2's excellent oxygen storage-release capacity, NH_3 adsorption was weakened, in comparison to the 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst. If NO_x were to be pre-adsorbed in the catalyst, the formation of nitrate and nitro species would be difficult to desorb, which would greatly hinder the SCR reaction. All the findings concluded that NH_3-SCR worked mainly through the Eley-Rideal (E-R) mechanism.

Keywords: in situ DRIFTS; V_2O_5-CeO_2/TiO_2-ZrO_2; catalysts; NH_3-SCR mechanism; NO_x; adsorption

1. Introduction

Generally, nitrogen oxides (NO_x), which may cause environmental problems, such as: Photochemical smog; acid rain; ozone depletion; and, health hazards, are mainly emitted from the industrial combustion of fossil fuels. Therefore, the reduction of NO_x has become an important research field for atmospheric environmental control. Currently, the selective catalytic reduction (SCR) is the most promising method to reduce the emissions of NO_x [1,2]. The temperature window of the traditional V-W (Mo)/Ti catalyst is 300–400 °C, but in some coal-fired power plants, the temperature of exhaust gas is lower. In order to enhance the NO_x conversion rate, the exhaust gases were reheated, which caused a large waste of energy. The narrow temperature window restrained its application. Thus, many researchers redirected their study to focus on the catalyst, which has superior low-temperature activity.

The VO_x/TiO_2 system for SCR has been studied extensively in the past and a number of reaction mechanisms have been proposed. It is generally accepted that the Brønsted and Lewis

acid sites are essential for the reaction mechanism. Topsoe et al. [3] proposed a "Brønsted NH_4^+" mechanism over a V_2O_5-based catalyst, which has gained the majority of support in the literature. Arnarson et al. [4] observed the SCR reaction over the VO_3H/TiO_2 catalyst and demonstrated that the Brønsted acid site served to capture the NH_3 and increased the NH_4^+ stability (increased Brønsted acid strength), which impacted the catalytic rate in a negative direction. Marberger et al. [5] had a similar conclusion for the V_2O_5-WO_3/TiO_2 catalyst. That is, the Brønsted acid sites hardly contributed to the SCR activity and mainly served as an NH_3 pool to replenish the Lewis sites. NO reacted predominantly with NH_3 adsorbed in the Lewis acid sites at low temperatures. SCR reactions over Ce-based catalysts mainly followed two mechanisms, one is the Eley–Rideal mechanism (i.e., the reaction of gaseous NO with adsorbed NH_3 species), and the other is the Langmuir–Hinshelwood mechanism (i.e., the reaction of adsorbed NO_x with adsorbed NH_3 species on adjacent sites) [6]. While these two reaction pathways probably do not exclude each other, it is essential to understand whether either or both species are relevant. Vuong et al. [7] reported that NH_3-SCR proceeded from a Langmuir–Hinshelwood mechanism on bare supports (TiO_2), while an Eley–Rideal mechanism operated on V-containing catalysts.

In recent years, cerium oxides have attracted extensive attention due to their outstanding oxygen storage-release capacity and excellent redox properties in the low-temperature NH_3-SCR reactions [8–10]. In $V/Ce_{1-x}Ti_xO_2$ catalysts, Ce-O sites are effectively covered by VO_x species, which hinder the formation of surface nitrates and cause the switch in the reaction mechanism. Zhang et al. [11] observed the adsorption and reaction processes in DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra and concluded that the cis-$N_2O_2^{2-}$ formed on CeO_2 reacted more favorably with NH_3 than with other nitrate species. Galvez et al. [12] demonstrated that the SCR reaction over activated carbon supported the V_2O_5 catalysts (V_2O_5/AC) that took place between the adsorbed species of NH_3 on the Brønsted acid sites, and the NO molecules in the gaseous phase, following an Eley–Rideal (E–R) mechanism. In Yu et al. [13], the study proposed that the SCR reaction over Zr_3 $(PO_4)_2/CeO_2$-ZrO_2 proceeded via the combination of the adjacent, surface N_xO_y species, and the ads-NH_3 species by Langmuir-Hinshelwood (L-H) mechanism. Ma et al. [14] also observed the enhanced NH_3 activation and NO_3-formation. The latter promoted the reaction of ads-NH_3 and ads-NO_3-species for the SCR reaction over N_bO_x/CeO_2-ZrO_2 catalysts—according to the "L-H" mechanism. Getting to know the reaction pathway and proposing reaction mechanisms is helpful in guiding the design and preparation of the catalysts [15].

In our previous study [9,16], a series of 1 wt. % V_2O_5-CeO_2/TiO_2-ZrO_2 catalysts with different contents of CeO_2were prepared by an impregnation method. It was found that the sample of Ce/Ti = 0.2 (the molar ratio) exhibited a favorable performance with a 92% NO_x conversion rate at 250 °C. In addition, the effect of Ce modification on microscopic properties and the catalytic performance of V_2O_5/TiO_2-ZrO_2 were investigated in more detail. It concluded that the promotional effect of adding Cemainly laid in the intensified interaction between the metal oxide components and the larger amount of Brønsted and Lewis acid sites, as well as the formation of active intermediates (-NH_2). In this study, we further investigated the NH_3-SCR mechanism over the optimal 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst, and by carrying out transient activity tests and in situ DRIFTS analyses under various conditions of single or mixing feeding gas and pre-treatment ways, proposed a possible reaction pathway.

2. Results and Discussion

2.1. Adsorption and Desorption Properties of NO_x and NH_3 on the Catalysts

The adsorption-desorption behavior of the catalyst is considered to be a crucial step to a heterogeneous catalysis system. To study the desorption status of the reactant gas on the catalyst surface, the desorption of NO on 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 was studied. As shown in Figure 1, the band at 3670 cm^{-1} was attributed to O-H, and it decreased with the increased temperature until the

negative peak appeared. The band at 3203 cm^{-1} was the result of the hydroxyl vibration. The catalysts contained a little bit of water at a normal temperature, and the water evaporated as the temperature rose; adsorption bands then disappeared. The bands (1618 cm^{-1}, 1367–1378 cm^{-1}, 1245–1288 cm^{-1}, 1130 cm^{-1}, and 1058 cm^{-1}) were ascribed to the adsorbed NO_x, especially the band of 1618 cm^{-1} which was related to weak adsorption of NO and NO_2 [16–18]. In the case of cis-$N_2O_2^{2-}$, bands should appear in the 1300–1400 cm^{-1} [19]. When the temperature exceeded 200 °C, $N_2O_2^{2-}$ appeared in the region of 1367–1378 cm^{-1} and the intensity of peaks increased as the temperature rose. This confirmed that it could exist stably on the surface of the catalyst. The band at 1245 cm^{-1} was due to bridging nitrate; the adsorption intensity receded as the temperature rose, and the band region moved to 1288 cm^{-1} with the generation of monodentate nitrate [17,20,21]. Subsequently, this peak disappeared as the temperature reached 400 °C. The band at 1130 cm^{-1} was assigned to nitrosyl NO^-, which could be oxidized to nitrite and nitrate with the existence of oxygen, and it sharply decreased as the temperature increased [22,23]. The band at 1054 cm^{-1} corresponded to nitrate species, which could exist on the surface of the catalyst stably and was hard to desorb even when the temperature was raised.

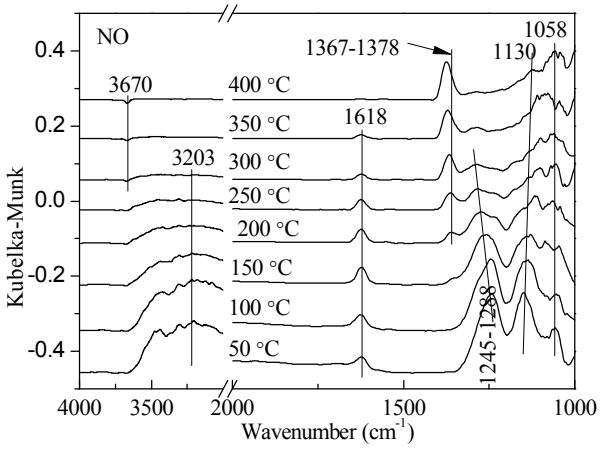
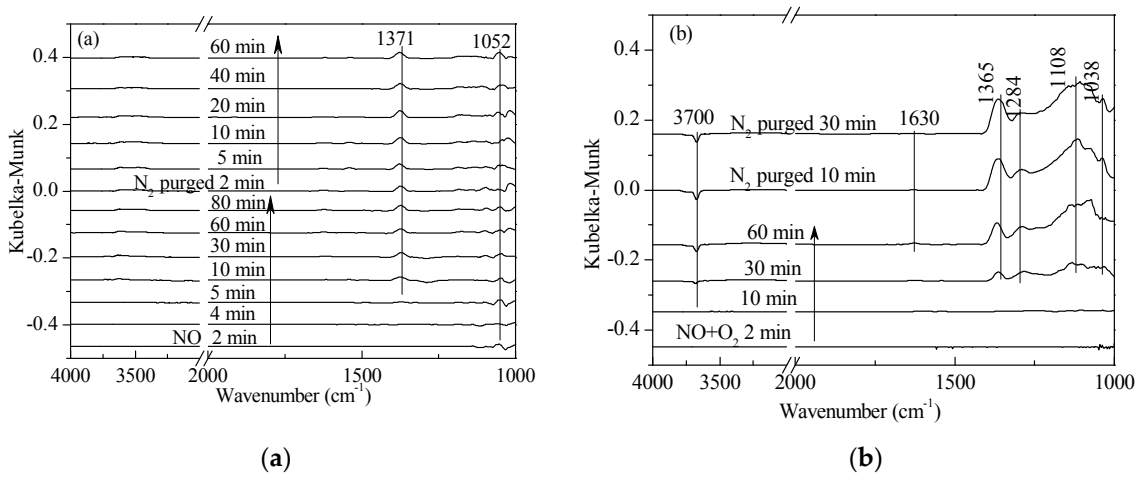


Figure 1. In situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra of NO desorption on 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 as a function of temperature after the catalyst was exposed to a flow of 800 ppm NO for 60 min at 25 °C.

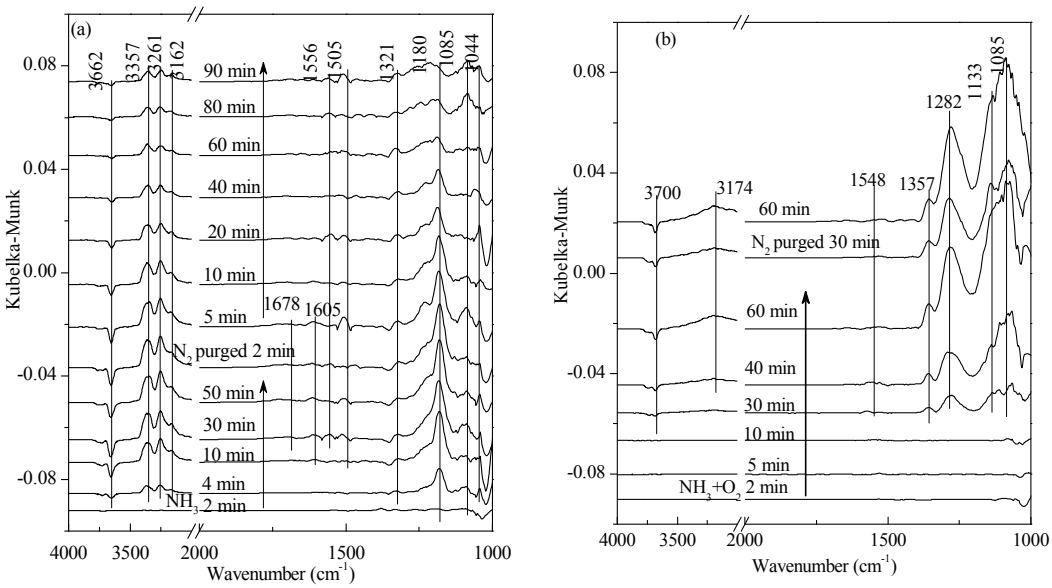
As shown in Figure 2a, as N_2 was steadily purged on, it was clear that the adsorption of NO was very weak at 250 °C, and $N_2O_2^{2-}$ and nitrate species only appeared at the band of 1371 cm^{-1} and 1052 cm^{-1}. In addition, there was no significant change in peak intensity by increasing the adsorption and desorption time, indicating that it could exist stably on the surface of the catalyst. As shown in Figure 2b, it was observed that the presence of O_2 obviously strengthened the adsorption intensity of NO_x on the surface of catalysts. After being exposed to NO + O_2 for 60 min, weak adsorption of NO and NO_2 appeared at the band of 1630 cm^{-1}. The bands at 1365 cm^{-1} and 1108 cm^{-1} could be assigned to cis- and trans-$N_2O_2^{2-}$ [19,24], respectively. Simultaneously, the bands at 1284 cm^{-1} and 1038 cm^{-1} were attributed to monodentate nitrate and nitrate species, respectively.



(**a**) (**b**)

Figure 2. In situ DRIFTS spectra of (**a**) NO adsorption and (**b**) NO + O_2 adsorption on 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2catalysts with N_2 purging for various time at 250 °C after the catalysts were exposed to a flow of 800 ppm NO or 800 ppm NO + 5% O_2 for 60 min.

As shown in Figure 3, the adsorption peaks of free O-H appeared at 3662 cm^{-1} and 3700 cm^{-1}, and the band at 3100–3400 cm^{-1} was associated with the N-H stretching vibrations, which are linked to Lewis acid sites. The peaks at 1556 cm^{-1}, 1548 cm^{-1}, and 1505 cm^{-1} corresponded to the formation of intermediate species (-NH_2) in SCR reactions [21]. In addition, there was no significant change in peak intensity as adsorption and desorption time increased. According to our previous study [16], intermediate species (-NH_2) were detected above 300 °C over the V_2O_5/TiO_2-ZrO_2 catalyst. The V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst exhibited more -NH_2 at lower temperatures, which explained its higher activity in comparison to other catalysts. Vuong et al. [11] collected different DRIFTS spectra of bare supports (CeO_2, TiO_2 and CeO_2-TiO_2) and supported vanadium catalysts (V/CeO_2, V/CeO_2-TiO_2 and V/TiO_2) at 200 °C. They reported additional bands at 1510–1520 cm^{-1} of NH_2, which were only observed on pure CeO_2 and CeO_2-TiO_2. It could be speculated that the addition of Ce was the key factor to affect the surface adsorbed NH_3 species. At the same time, the peaks at 1605 cm^{-1}, 1357 cm^{-1}, 1321 cm^{-1}, 1282 cm^{-1}, 1180 cm^{-1}, and 1133 cm^{-1} were associated with NH_3 cooperating vibration—linked to Lewis acid sites [25,26]. According to our previous study [16], with the addition of Ce, the acid sites of the catalysts increased and the optimal V_2O_5-0.2CeO_2/TiO_2-ZrO_2 sample possessed the largest amount of surface acid sites, which greatly promoted the SCR reaction. The same trend was observed in Vuong et al. [7]. They demonstrated that the relative amount of Lewis acid sites in the V-containing catalysts decreased in the order V/$Ce_{0.5}Ti0_{0.5}O_2$ > V/CeO_2 > V/TiO_2. The band at 1180 cm^{-1} in Figure 3a split into two NH_3 adsorption peaks (1085 cm^{-1} and 1044 cm^{-1}), and the band at 1133 cm^{-1} in Figure 3b corresponded to the peak at 1085 cm^{-1}. The band at 1678 cm^{-1} was associated with NH^{4+} symmetric vibration and is linked to Brønsted acid sites [27,28]. Comparing Figure 3a with Figure 3b, it can be found that the presence of O_2 hindered the adsorption of NH_3. However, in Figure 3b, after the feeding of NH_3 + O_2 was stopped, the intensity of the NH_3 adsorption peak, linked to Lewis acid sites, was stronger than in Figure 3a. It might have been caused by the re-adsorption of desorbed ammonia or weak ammonia adsorption on Lewis acid sites, because CeO_2 had the capacity of oxygen storage-release and O_2 occupied some active sites.



(**a**) (**b**)

Figure 3. In situ DRIFTS spectra of (**a**) NH_3 adsorption and (**b**) NH_3 + O_2 adsorption on V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalysts with N_2 purging for various time at 250 °C after the catalysts were exposed to a flow of 800 ppm NH_3 or 800 ppm NH_3 + 5% O_2 for 60 min.

2.2. Transient Response Experiment Analysis

In order to illuminate the difference between NO_x species and explain the SCR reaction mechanism, transient reaction studies by in situ DRIFTS spectra were performed. As shown in Figure 4, the NH_3 adsorption peak could be found after NH_3 and NO were introduced for two min. After adsorption was saturated, the bands at 3400 cm^{-1}, 3100 cm^{-1}, and 1198 cm^{-1} were associated with NH_3 adsorption and was linked to Lewis acid sites. The intermediate species (-NH_2) appeared at 1591 cm^{-1}, which implied more active intermediates for the NH_3 oxidation reaction. No obvious NO_x adsorption was observed; it was a preliminary inference that SCR reactions mainly followed from the Eley–Rideal mechanism.

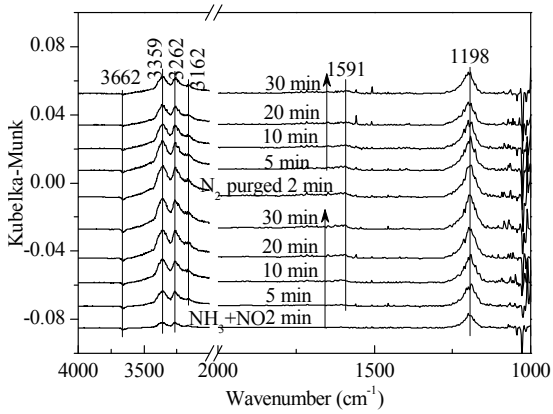
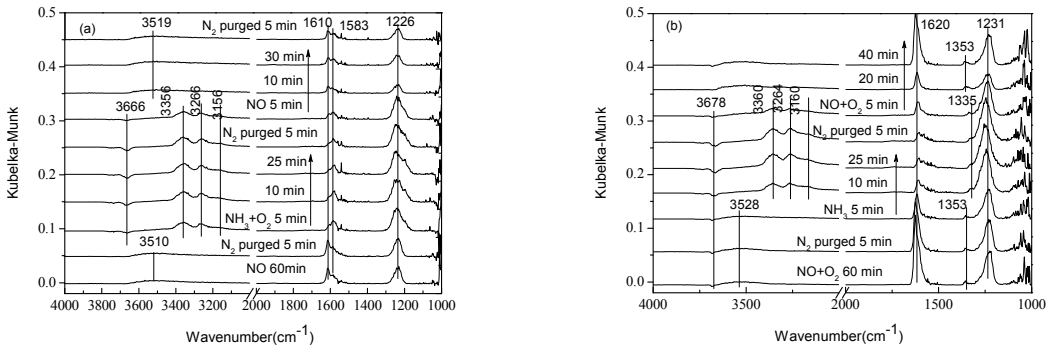


Figure 4. In situ DRIFTS spectra of NH_3 + NO adsorption on 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalysts with N_2 purging for various times at 250 °C after the catalysts were exposed to a flow of 800 ppm NH_3 and 800 ppm NO for 60 min.

As shown in Figure 5, catalysts were exposed to the flow of NO and NO + O_2 at 250 °C for 60 min. The O-H adsorption peaks appeared at 3510 cm^{-1} and 3528 cm^{-1}. The N-H stretching vibration

peaks appeared in the range of 3400–3100 cm^{-1} after NO was introduced for two min. However, in Figure 5b, NH_3 adsorption peaks appeared after NH_3 was introduced for 10 min in the same region. NO_2 asymmetric vibration adsorption peaks appeared at 1610 cm^{-1} and 1620 cm^{-1} in Figure 5a,b, respectively. The bands at 1583 cm^{-1}, 1226 cm^{-1}, and 1231 cm^{-1} were ascribed to bridging nitrates. cis-$N_2O_2^{2-}$ appeared at 1353 cm^{-1} in Figure 5b, and it shifted to the region of 1335 cm^{-1} with the introduction of NH_3, which then weakened the adsorption. When introducing NO + O_2 again, the adsorption peak recovered to 1353 cm^{-1}.



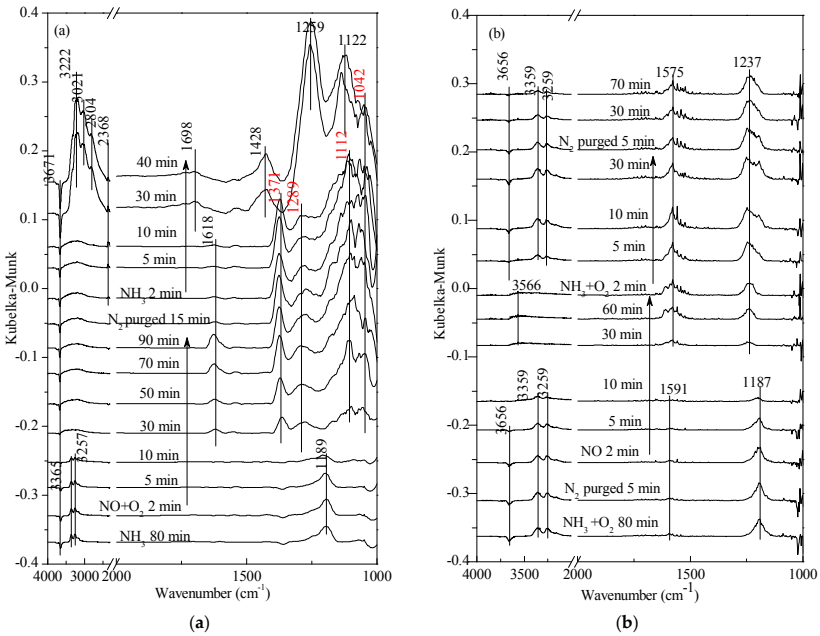
(**a**) (**b**)

Figure 5. In situ DRIFTS spectra of the transient reactions at 250 °C between (**a**) NO and pre-adsorbed NH_3 + O_2 and (**b**) NH_3, and pre-adsorbed NO + O_2 species over 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalysts recorded as a function of time.

NH_3 had no obvious influence on the NO_x adsorption peak at 2000–1000 cm^{-1}, especially after being exposed to NO + O_2 where the influence became tinier. After the pre-adsorption of NO, the intensity of the NO_x adsorption peak was obvious, but NH_3 adsorption could barely be found. With the introduction of NH_3, the N-H stretching vibration was present in the range of 3400–3100 cm^{-1}, as seen in both Figure 5a,b. The results showed that when NO + O_2 was injected separately, NO + O_2 occupies SCR active reaction sites and restrains the adsorption of NH_3, before hindering the SCR reaction. When NO and NO + O_2 was reintroduced, respectively, peaks located at 3519 cm^{-1} and assigned to O-H adsorption were observed. The intensity of the NO_x adsorption peak had no decrement; on the contrary, NH_3 adsorption, which was linked to Lewis acid sites, disappeared. These results indicated that the gas-phase NO_x had reacted with NH_3 on Lewis acid sites, which verified the Eley–Rideal mechanism on catalysts. However, in Chen et al. [29], a Langmuir–Hinshelwood mechanism operated on the CeTi catalyst, and adsorbed NH_3 and NH_4^+ that reacted with NO/O_2 from the gas phase. Vuong et al. [7] demonstrated that the switch in reaction mechanisms has its roots in the structural differences of catalysts and supports. In V/$Ce_{1-x}Ti_xO_2$ catalysts, Ce-O sites are effectively covered by VO_x species, which hinders the formation of surface nitrates and causes the switch in the reaction mechanism.

As shown in Figure 6a, when NO + O_2 is introduced, the adsorption peaks at the region of 3400–3100 cm^{-1} and 1189 cm^{-1} disappeared, while the O-H adsorption peak (1618 cm^{-1}), the $N_2O_2^{2-}$ adsorption peak (1371 cm^{-1} and 1112 cm^{-1}), and the nitrate species peak (1024 cm^{-1}) appeared. When NH_3 was introduced again, the NO_2 adsorption peak disappeared. Moreover, a strong adsorption of NH_3 appeared at the region of 3400−3100 cm^{-1} and 1259 cm^{-1}. Brønsted acid adsorption appeared at 1698 cm^{-1} and 1428 cm^{-1} and considerably intensified, while other NO_x adsorption had no obvious change.

As shown in Figure 6b, NO was introduced after being exposed to NH_3 + O_2. Bridging nitrate and monodentate nitrate appeared at 1575 cm^{-1} and O-H vibration appeared at 3566 cm^{-1}. When NH_3 + O_2were introduced again, the O-H vibration became stronger and the NH_3 adsorption peak at the region of 3400–3100 cm^{-1} was heavily weakened, as compared with that in Figure 6a. As a result, it can be concluded that O_2 reacted with NO first.



(**a**) (**b**)

Figure 6. In situ DRIFTS spectra of the transient reactions at 250 °C between (**a**) NO + O_2 and pre-adsorbed NH_3, and (**b**) NO and pre-adsorbed NH_3 + O_2 species over 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalysts recorded as a function of time.

In Figure 7, NH_3 was introduced first, and then NO was introduced in combination with NH_3. Lastly, O_2 was also introduced with NH_3, NO, and O_2 being presented at the same time. In these three different atmospheres, the intensity of NH_3 adsorption on Lewis acid sites had no change. Meanwhile, the active intermediate species of -NH_2 appeared at 1588 cm^{-1}, indicating that NH_3 molecules continued to be adsorbed on the catalytic surface with the process of reaction. The stable existence of intermediate species (-NH_2) explained the high SCR activity of the V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst at low temperatures. Simultaneously, the intensity of the O-H negative peak receded gradually, which might have been caused by the H_2O produced in the SCR reaction.

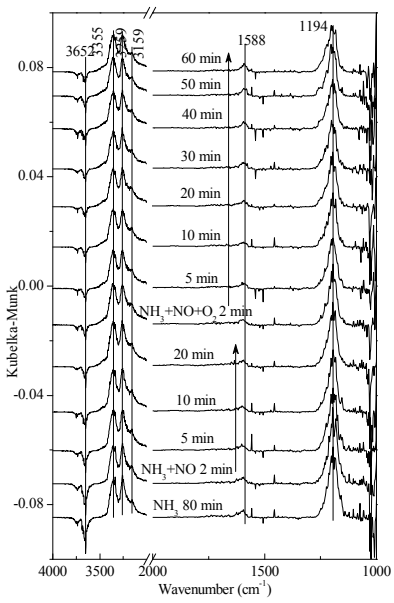
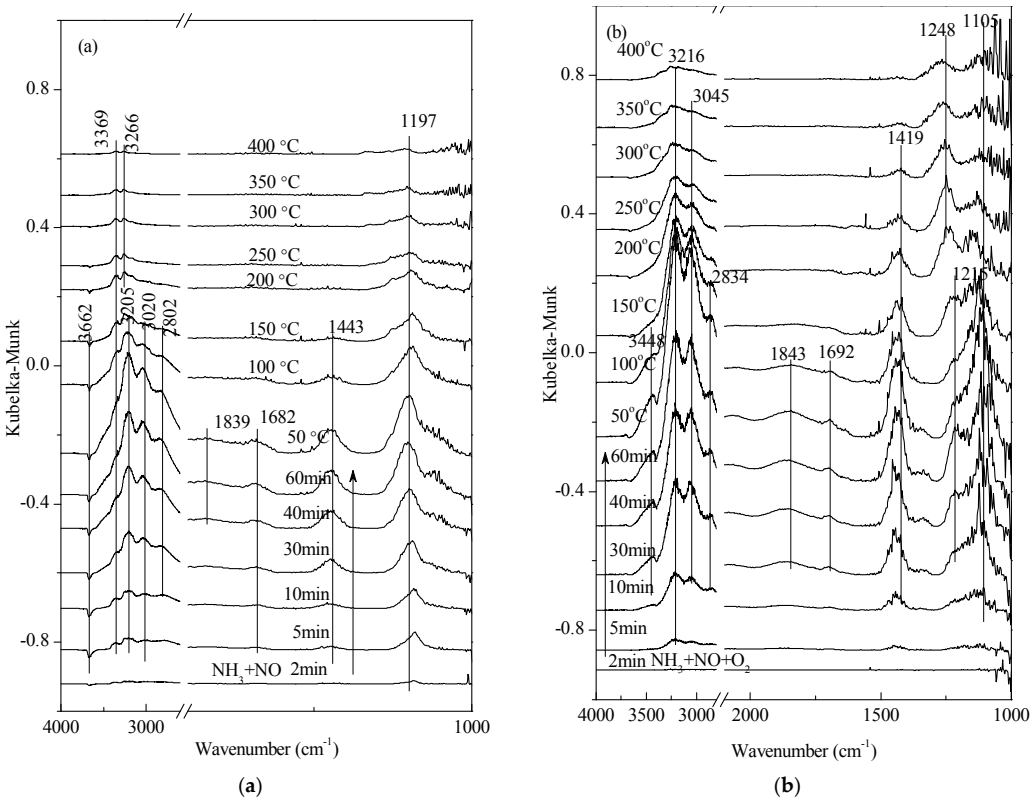


Figure 7. In situ DRIFTS spectra of NH_3 + NO + O_2 pre-adsorption transient reaction at 250 °C over 1 wt. %V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalysts recorded as a function of time.

2.3. Steady-State Response Experiments

As shown in Figure 8, catalysts were saturated at 25 °C after 60 min pre-adsorption. -NO_2 adsorption appeared at 1839 cm^{-1} and 1843 cm^{-1}. The bands at 1692 cm^{-1}, 1682 cm^{-1}, 1443 cm^{-1}, and 1419 cm^{-1} were associated with NH_4^+ adsorption, linked to Brønsted acid sites, and the bands of 3400–3100 cm^{-1},1197 cm^{-1}, and 1215 cm^{-1} were associated with NH_3 adsorption, linked to Lewis acid sites. As shown in Figure 8b, $N_2O_2^{2-}$ species appeared at 1106 cm^{-1} with the presence of O_2, which indicated that the existence of O_2 would promote NO adsorption. Comparing Figure 8a with Figure 8b, NH_3 adsorption became much stronger with the existence of O_2. At the same time, the combination of NO_x and NH_3 appeared at 1248 cm^{-1}, and $N_2O_2^{2-}$ species decreased with increasing temperatures, indicating that O_2 is essential for SCR reactions.



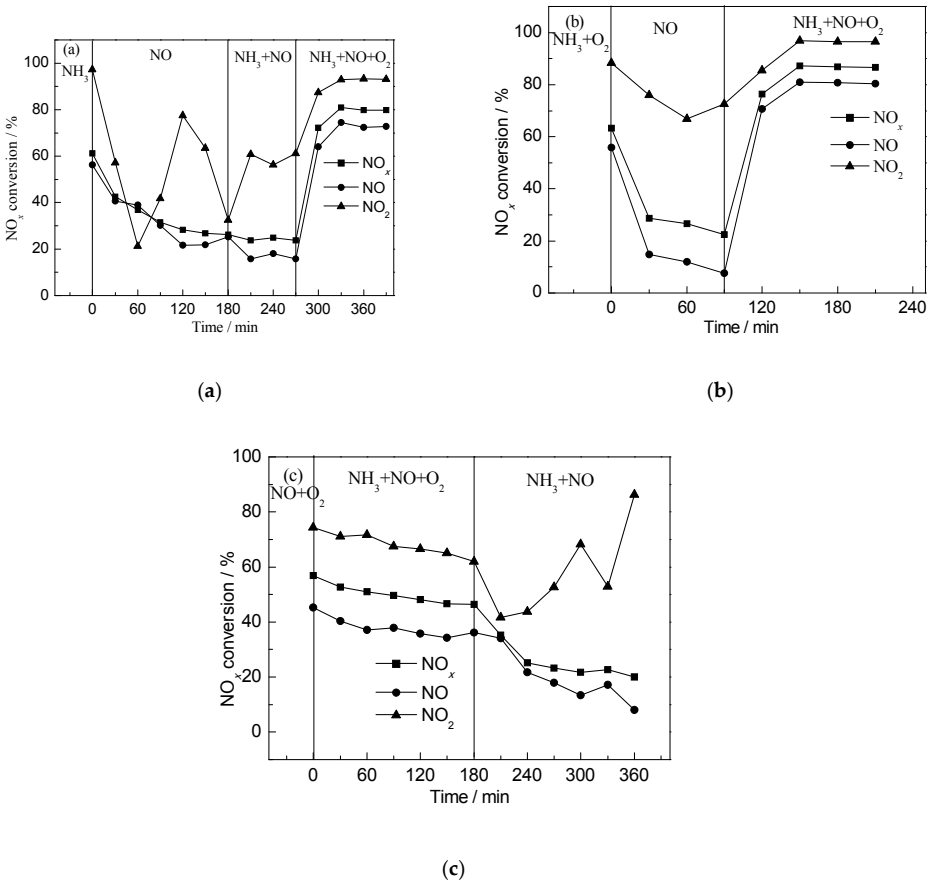
(**a**) (**b**)

Figure 8. In situ DRIFTS spectra of (**a**) NH_3 + NO desorption and (**b**) NH_3 + NO + O_2 desorption on 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 as a function of temperature after the catalyst was exposed to a flow of 800 ppm NO, 800 ppm NH_3, and 5% O_2 for 60 min at 25 °C.

2.4. Transient SCR Activity Test Experiments

As shown in Figure 9a, NO was introduced after the pre-adsorption of NH_3 for 2 h. The initial conversion of NO_x, NO, and NO_2 was 61%, 56%, and 97%, respectively. With a steady flow of NO_x, adsorbed ammonia was consumed gradually and the conversion of NO_x and NO decreased, while NO_2 conversion went down-up-down. According to the in situ DRIFTS results, it might be that NO_2 is easier to be adsorbed on the catalysts surface, thus leading to the decrease of NH_3 adsorption; the conversion of NO_2 dropped correspondingly. Until NH_3 was completely consumed, NO_2 started to be adsorbed on catalysts and the conversion went up, and decreased again after adsorption saturation. By feeding NH_3 and NO simultaneously, the conversion rate of NO_x and NO was lower than if only NO was fed, suggesting that NO_2 occupied active reaction sites resulting in its poor performance. In the case of feeding NH_3 and NO at the same time, we found that all the three conversion rates showed the same trend, namely, that the conversion rate reduced after the first rose, which is associated

with the promotion of NH_3 for SCR reaction. When the three gases: NH_3; NO; and, O_2 were fed synchronously, the NO_x conversion rate reached a stable level of 80%. Simultaneously, the conversion rate of NO and NO_2 stabilized at 73% and 92%, respectively. What is more, both conversion rates obviously increased, indicating that NO_2 was easier to be reduced. We can conclude that O_2 was essential for the SCR reaction.



(**a**) (**b**)

(**c**)

Figure 9. Transient SCR (selective catalytic reduction) activity tests (250 °C) under different pre-adsorption conditions: (**a**) pre-adsorption of NH_3; (**b**) pre-adsorbed of NH_3 and O_2 and (**c**) pre-adsorption of NO + O_2.

In Figure 9b, NO was introduced after NH_3 and O_2 was pre-adsorbed for 2 h. It was obvious that the conversion rate of NO_x reduced compared to Figure 9a. However, the conversion rate of NO_2 increased and the conversion rate of NO decreased. This might have been caused by the pre-adsorbed O_2 reacting with NO and producing NO_2, which was easier to react with, and be adsorbed by, the catalysts. The conversion rate increased rapidly when NH_3, NO, and O_2 was present at the same time.

In Figure 9c, after the pre-adsorption of NO + O_2 for 2 h, the denitration efficiency declined continuously with the existence of NH_3, NO, and O_2. When introducing NH_3 and NO together, the conversion rate of NO_x and NO went down-up-down, while the conversion rate of NO_2 went down-up-down-up. This could be ascribed to the oxygen storage-release capacity of CeO_2. NO adsorbed on the catalysts, reacted with O_2, and produced NO_2, resulting in the ascended e-conversion rate of NO_2. When O_2 was completely consumed, the conversion rate went down again. In this process, the SCR reaction was very weak. As a result, most of the NO_2 adsorbed on the catalysts, so its conversion rate went up. After this, O_2 reacted with NO and produced more NO_2, and its conversion rate declined after the adsorption of NO_2 was saturated. When O_2 reacted with NO completely, NO_2 occupied the adsorption sites of O_2, leading to the conversion rate going

up. The combined effect of the NO_2 and NO conversion rate resulted in the conversion of NO_x going down-up-down-up.

2.5. Low-Temperature SCR Reaction Pathway

The above analyses of in situ DRIFTS have demonstrated the relatively high ability of 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst on NH_3 adsorption and oxidation. At the reaction temperature (250 °C), the Lewis acid sites were much more stable than were the Brønsted acid sites and the quantity of coordinated NH_3 was larger than that of the NH^{4+} ions. The gaseous NH_3 was adsorbed on the catalytic surface, followed by a reaction with the gas phase NO to form the intermediate of NH_2NO, which was unstable and would decompose into N_2 and H_2O (Eley–Rideal mechanism). Based on the combination of in situ DRIFTS experiments and transient SCR activity tests, the mechanism of NH_3-SCR reaction over V_2O_5-CeO_2/TiO_2-ZrO_2 catalysts are mainly as followed:

$$O_2 + 2^* \rightarrow 2O^{-*} (* : \text{surface activesites}) \quad (1)$$

$$NH_3(g) \overset{Ce^{4+}}{\rightarrow} NH_3(\alpha)(\text{Lewis acid site}) \quad (2)$$

$$NH_3(\alpha) + O^{-*} \rightarrow NH_2(\alpha) + OH(\alpha) \quad (3)$$

$$NH_2(\alpha) + NO(g) \rightarrow NH_2NO(\alpha) \rightarrow N_2(g) + H_2O(g) \quad (4)$$

3. Materials and Methods

3.1. Catalyst Preparation

The Ti-Zr support (molar ratio of Ti:Zr = 1:1) was prepared by a co-precipitation method. Typically, an equal molar amount of $TiCl_4$ solution and $ZrOCl_2 \cdot 8H_2O$ was dissolved in the deionized water. $NH_3 \cdot H_2O$ solution was dropped into a stoichiometric solution of $TiCl_4$ and $ZrOCl_2 \cdot 8H_2O$ with steady stirring until the pH reached 10. The obtained precipitation solution was aged in air for 24h at room temperature, and then washed with deionized water until the supernatant was free from Cl^-. Subsequently, the resulting paste was dried at 110 °C for 12 h and then calcined at 450 °C for 4 h in a muffle stove.

1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 samples were prepared by the step-by-step impregnation of Ti-Zr and $CeNO_3 \cdot 6H_2O$ (Ce/Ti = 0.2, molar ratio). The obtained mixture was stirred for 2 h at 25 °C, and then for about 4 h at 85 °C until the water boiled away. The resulting precipitate was dried at 110 °C for 12 h, followed by being calcined at 450 °C for 4 h in a muffle stove to obtain intermediate CeO_2/Ti-Zr, which was then impregnated with a NH_4VO_3 solution. The obtained mixture was dried and calcined in the same process of preparing CeO_2/Ti-Zr samples to finally acquire 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 samples.

3.2. In situ DRIFTS Experiments

In situ DRIFTS investigations were carried out on a Nicolet 6700 spectrometer (Thermo Electron Corporation, Waltham, MA, USA), running in the wavenumber range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. A thin, intact and self-supporting wafer of adsorbents were prepared and mounted inside a high temperature cell (HTC-3, Harrick Scientific Corporation, Ithaca, NY, USA). Prior to each experiment, the catalyst was heated to 400 °C under an N_2 atmosphere for 1h to remove any adsorbed species, then cooled down to the reaction temperature. The background spectrum was recorded in N_2 flow and was automatically subtracted from the sample spectrum during the experiment. Then the N_2 flow was switched to a stream containing one or more reactants, such as NH_3, NO, and O_2. In situ DRIFTS experiments included transient response and steady-state response experiments. It should be noted that new catalyst samples pretreated under the same conditions and were used in each in situ DRIFTS experiments.

3.3. Transient SCR Activity Tests

As shown in Table 1, in order to coordinate the in situ DRIFTS experiments, catalyst activity test experiments were designed under different conditions of feeding gases. A total of 0.3 g of catalyst (screening through 40 to 60 mesh sieve) was tested on a fixed-bed quartz tube reactor (Nanjing University of Technology, Nanjing, China)with an internal diameter of 7 mm at the temperature of 250 °C. The total flow rate was 100 mL/min, which was pre-mixed in a gas mixer to obtain the simulated gas containing 0.08% NO, 0.08% NH_3, and 5% O_2, with a balance of N_2, NO, NO_2, and NO_x in the outlet, which was continually monitored by a flue gas analyzer (Testo 330-2 LL, Shanghai, China). Typically, during the experiments, about 5% NO was converted to NO_2. In other words, 5% NO_x existed in the form of NO_2.

Table 1. The working conditions of transient SCR activity tests.

Gas Composition	1	2	3	4
I	NH_3	NO	NH_3 + NO	NH_3 + NO + O_2
II	NH_3 + O_2	NO	NH_3 + NO + O_2	-
III	NO + O_2	NH_3 + NO + O_2	NH_3 + NO	-

4. Conclusions

In situ DRIFTS experiments and transient SCR activity tests were used coordinately to observe active and intermediate species and to describe the possible reaction path of 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 at low temperature. The results are as followed:

(1) NH_3 held a dominant position in the competitive adsorption between NH_3 and NO. Transient SCR activity tests showed that the NH_3 pre-adsorbed catalyst exhibited better SCR activity than its NO_x pre-adsorbed counterpart.

(2) NO might be adsorbed on the catalyst surface and be converted to monodentate nitrite and nitrate species, which is more obvious in the presence of O_2, and dramatically restrains the adsorption of NH_3, hindering the SCR reaction.

(3) More acid sites and reaction intermediate species -NH_2 at lower temperatures mainly led to the higher activity of the V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst.

(4) Transient SCR activity tests and steady-state response experiments both confirmed that NH_3-SCR activity was enhanced by the presence of O_2. NH_3 adsorption intensity had no obvious difference, whether NO or O_2 was introduced or not, indicating that the adsorption and consumption of NH_3 was in dynamic equilibrium, which promoted SCR reaction.

(5) NH_3-SCR reaction over 1 wt. % V_2O_5-0.2CeO_2/TiO_2-ZrO_2 catalyst mainly follows the E-R mechanism.

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