In Situ DRIFTS Studies of NH$_3$-SCR Mechanism over V$_2$O$_5$-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$_2$O$_5$ and 0.2 CeO$_2$ (the Mole ratio of Ce to Ti-Zr) was impregnated to obtain the V$_2$O$_5$-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$_2$O$_5$-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$_2$O$_5$-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$_2$O$_5$-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$_3$/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$_2$O$_5$-based catalyst, which has gained the majority of support in the literature. Arnarson et al. [4] observed the SCR reaction over the VO$_3$H/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$_2$O$_5$-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/($\text{Ce}_{1-x}\text{Ti}_x$)O$_2$ 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$_2$O$_2^{2-}$ 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$_2$O$_5$ catalysts (V$_2$O$_5$/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$_2$O$_y$ 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$_2$O$_y$/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$_2$O$_5$-CeO$_2$/TiO$_2$-ZrO$_2$ catalysts with different contents of CeO$_2$ were 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$_2$O$_5$/TiO$_2$-ZrO$_2$ were investigated in more detail. It concluded that the promotional effect of adding Ce mainly 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$_2$O$_5$-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$_2$ 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$_2$O$_5$-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\(_2\)O\(_2\)\(^{2-}\), bands should appear in the 1300–1400 cm\(^{-1}\) [19]. When the temperature exceeded 200 °C, N\(_2\)O\(_2\)\(^{2-}\) 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\(_x\), 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](image-url)  
**Figure 1.** In situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra of NO desorption on 1 wt. % V\(_2\)O\(_5\)-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\(_2\)O\(_2\)\(^{2-}\) 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\(_2\)O\(_2\)\(^{2-}\) [19,24], respectively. Simultaneously, the bands at 1284 cm\(^{-1}\) and 1038 cm\(^{-1}\) were attributed to monodentate nitrate and nitrate species, respectively.
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$^{-1}$, 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$^{-1}$ and 1180 cm$^{-1}$ in Figure 3a split into two NH$_3$ adsorption peaks (1085 cm$^{-1}$, 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$_2$O$_5$-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$_0.5$Ti$_0.5$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 vibrational 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.
The O-H adsorption peaks appeared at 3510 cm$^{-1}$ and 3528 cm$^{-1}$. The N-H stretching vibration was observed; it was a preliminary inference that SCR reactions mainly followed from the Eley–Rideal mechanism.

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.

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 was linked to Lewis acid sites. The intermediate species (-NH$_2$) appeared at 1591 cm$^{-1}$.

![Figure 3](image_url) In situ DRIFTS spectra of (a) NH$_3$ adsorption and (b) NH$_3$ + O$_2$ adsorption on V$_2$O$_5$-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$_3$ or 800 ppm NH$_3$ + 5% O$_2$ for 60 min.

![Figure 4](image_url) In situ DRIFTS spectra of NH$_3$ + NO adsorption on 1 wt. % V$_2$O$_5$-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.
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$_2$O$_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$^{-1}$.

![Figure 5](image)  
*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$_2$O$_5$-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$_2$ 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$_2$ 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$_x$O$_2$ 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$_2$O$_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$^{-1}$. Bronsted 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$_2$ were 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.
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$_2$O$_5$-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$_2$O produced in the SCR reaction.

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$_2$O$_5$-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$_2$O produced in the SCR reaction.
2.3. Steady-State Response Experiments

As shown in Figure 8, catalysts were saturated at 25 °C after 60 min pre-adsorption. NO 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\(_2\)O\(_2^{2-}\) 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\(_2\)O\(_2^{2-}\) species decreased with increasing temperatures, indicating that O\(_2\) is essential for SCR reactions.

![a](a) ![b](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\(_2\)O\(_5\)-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.

![Figure 9](image)

**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$_3$ 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$_2$ were 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$_3$ 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$_2$O$_5$-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 Bronsted 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$_2$NO, which was unstable and would decompose into N$_2$ and H$_2$O (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$_2$O$_5$-CeO$_2$/TiO$_2$-ZrO$_2$ catalysts are mainly as followed:

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

$$\text{NH}_3(g) \xrightarrow{\text{Ce}^{4+}} \text{NH}_3(\alpha)(\text{Lewis acid site}) \quad (2)$$

$$\text{NH}_3(\alpha) + O^{*-} \rightarrow \text{NH}_2(\alpha) + \text{OH}(\alpha) \quad (3)$$

$$\text{NH}_2(\alpha) + \text{NO}(g) \rightarrow \text{NH}_2\text{NO}(\alpha) \rightarrow \text{N}_2(g) + \text{H}_2\text{O}(g) \quad (4)$$

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$_2$·8H$_2$O was dissolved in the deionized water. NH$_3$·H$_2$O solution was dropped into a stoichiometric solution of TiCl$_4$ and ZrOCl$_2$·8H$_2$O with steady stirring until the pH reached 10. The obtained precipitation solution was aged in air for 24 h 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$_2$O$_5$-0.2CeO$_2$/TiO$_2$-ZrO$_2$ samples were prepared by the step-by-step impregnation of Ti-Zr and CeNO$_3$·6H$_2$O (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$_4$VO$_3$ 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$_2$O$_5$-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 1 h 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       |
|-----------------|------------|---------|---------|---------|
|                 | 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\(_2\)O\(_5\)-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\(_2\)O\(_5\)-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\(_2\)O\(_5\)-0.2CeO\(_2\)/TiO\(_2\)-ZrO\(_2\) catalyst mainly follows the E-R mechanism.

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