Recent Progress on Improving Low-Temperature Activity of Vanadia-Based Catalysts for the Selective Catalytic Reduction of NO\textsubscript{x} with Ammonia

Zhihua Lian\textsuperscript{1}, Yingjie Li\textsuperscript{1,2}, Wenpo Shan\textsuperscript{1,*} and Hong He\textsuperscript{1,2,3,*}

\textsuperscript{1} Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China; zhlian@iue.ac.cn (Z.L.); yjli@iue.ac.cn (Y.L.)
\textsuperscript{2} University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{3} State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

\* Correspondence: wpshan@iue.ac.cn (W.S.); honghe@rcees.ac.cn (H.H.)

Received: 31 October 2020; Accepted: 1 December 2020; Published: 4 December 2020

Abstract: Selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) has been successfully applied to abate NO\textsubscript{x} from diesel engines and coal-fired industries on a large scale. Although V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}(MoO\textsubscript{3})/TiO\textsubscript{2} catalysts have been utilized in commercial applications, novel vanadia-based catalysts have been recently developed to meet the increasing requirements for low-temperature catalytic activity. In this article, recent progress on the improvement of the low-temperature activity of vanadia-based catalysts is reviewed, including modification with metal oxides and nonmetal elements and the use of novel supports, different synthesis methods, metal vanadates and specific structures. Investigation of the NH\textsubscript{3}-SCR reaction mechanism, especially at low temperatures, is also emphasized. Finally, for low-temperature NH\textsubscript{3}-SCR, some suggestions are given regarding the opportunities and challenges of vanadia-based catalysts in future research.

Keywords: selective catalytic reduction; vanadia-based catalysts; low-temperature activity; reaction mechanism

1. Introduction

Nitrogen oxides (NO\textsubscript{x}, including NO and NO\textsubscript{2}), primarily emitted from fossil fuel combustion in both stationary and mobile sources, are major pollutants in the atmosphere. NO\textsubscript{x} is harmful to human health and can lead to the greenhouse effect, ozone depletion, acid rain, photochemical smog, and haze. Therefore, reducing the emission of NO\textsubscript{x} has become one of the most urgent atmospheric environment problems [1–3]. Increasingly stringent policies and legislation to control the emission of nitrogen oxides have been enacted all over the world.

In the 1970s, selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) was first applied to NO\textsubscript{x} removal from stationary sources in Japan [4], and has subsequently been widely used all over the world for NO\textsubscript{x} control from both stationary and mobile sources [5]. The NH\textsubscript{3}-SCR process mainly comprises the following reactions:

\[
\begin{align*}
4\text{NO}(g) + 4\text{NH}_3(g) + \text{O}_2(g) & \rightarrow 4\text{N}_2(g) + 6\text{H}_2\text{O}(g) \\
2\text{NO}_2(g) + 4\text{NH}_3(g) + \text{O}_2(g) & \rightarrow 3\text{N}_2(g) + 6\text{H}_2\text{O}(g) \\
2\text{NO}(g) + 4\text{NH}_3(g) + 2\text{NO}_2(g) & \rightarrow 4\text{N}_2(g) + 6\text{H}_2\text{O}(g)
\end{align*}
\]
Catalysts are the key components in NH₃-SCR technology for abating NOₓ emission. Currently, V₂O₅-WO₃/TiO₂ is commercially applied because of its excellent catalytic performance at 300–400 °C and strong SO₂ resistance [6]. Due to the high operating temperature, the precipitator and desulfurizer units should be installed downstream of the SCR unit in power plants [7]. However, this results in deactivation of the catalysts by poisoning with heavy metals, phosphorus and alkali/alkaline earth metals existing in the stack gases. Furthermore, the flue gas temperature from steel, glass and cement plants is lower than the working temperature of traditional V-based catalysts [8]. In order to avoid rapid deactivation and the need for additional energy consumption and to satisfy increasingly stringent NOₓ emission limits, the study of novel low-temperature vanadia-based SCR catalysts with high performance is highly desirable and has attracted broad attention to the deNOₓ process. Figure 1 shows the numbers of papers published each year from 1991 to 2020 containing “vanadium” and “SCR” in their contents using the “web of science” search engine. The increasing trend in the number of publications reflects the popularity, importance and enthusiasm for research of the vanadia-based catalysts for NH₃-SCR.

\[
\begin{align*}
6\text{NO}(g) + 4\text{NH}_3(g) & \rightarrow 5\text{N}_2(g) + 6\text{H}_2\text{O}(g) \\
6\text{NO}_2(g) + 8\text{NH}_3(g) & \rightarrow 7\text{N}_2(g) + 12\text{H}_2\text{O}(g)
\end{align*}
\]

Catalysts are the key components in NH₃-SCR technology for abating NOₓ emission. Currently, V₂O₅-WO₃/TiO₂ is commercially applied because of its excellent catalytic performance at 300–400 °C and strong SO₂ resistance [6]. Due to the high operating temperature, the precipitator and desulfurizer units should be installed downstream of the SCR unit in power plants [7]. However, this results in deactivation of the catalysts by poisoning with heavy metals, phosphorus and alkali/alkaline earth metals existing in the stack gases. Furthermore, the flue gas temperature from steel, glass and cement plants is lower than the working temperature of traditional V-based catalysts [8]. In order to avoid rapid deactivation and the need for additional energy consumption and to satisfy increasingly stringent NOₓ emission limits, the study of novel low-temperature vanadia-based SCR catalysts with high performance is highly desirable and has attracted broad attention to the deNOₓ process. Figure 1 shows the numbers of papers published each year from 1991 to 2020 containing “vanadium” and “SCR” in their contents using the “web of science” search engine. The increasing trend in the number of publications reflects the popularity, importance and enthusiasm for research of the vanadia-based catalysts for NH₃-SCR.

Herein, this work reviews the latest progress, especially the progress in the last five years, on vanadia-based catalysts for low-temperature NH₃-SCR, including a summary of methods for improving the performance at low temperature over vanadia-based catalysts and a discussion of the reaction mechanism of low-temperature NH₃-SCR, and finally proposes suggestions for the development of vanadia-based catalysts with superior low-temperature SCR activity.

2. Performance Improvement at Low Temperatures

The narrow operating temperature window of vanadia-based catalysts restricts their broader applications in the deNOₓ process. Though catalysts with high loadings of V₂O₅ exhibit high catalytic activity, high vanadia content leads to a decrease in N₂ selectivity and thermal stability and an increase in the catalytic oxidation of sulfur dioxide to sulfur trioxide, which induces severe corrosion problems for equipment [9]. Therefore, researchers have devoted much effort to improving the low-temperature
catalytic activity of vanadia-based catalysts, including modification of the active components, supports, and preparation methods, and experimenting with metal vanadates and specific structures.

2.1. The Modification of Vanadia-Based Catalysts

There are many reports on the modification of vanadia-based catalysts with transition metal oxides or rare-earth oxides to promote low-temperature NH₃-SCR activity. V-based catalysts were modified with different transition metal (Co, Mn, Fe, Cu) oxides via the impregnation method, and Cu-V/TiO₂ was found to present the best catalytic performance at 225–375 °C, probably attributable to the increased abundance of active surface oxygen species and strong acid sites [10]. Cu-doped V₂O₅/WO₃-TiO₂ exhibited higher NOₓ conversion than a V/WTi sample, which was mainly attributed to the existence of double redox couples of Cu²⁺/Cu⁺ and V⁵⁺/V⁴⁺ from the adjacent copper oxides and vanadium oxides on the surface [11]. In a study of the effects of different CuO doping levels, 7 wt.% Cu/VWTi exhibited high SCR activity and Hg⁰ oxidation at 280–360 °C, resulting from high dispersion of active species and enhancement of the redox properties [12]. In addition, a 0.3 wt.% Ce-0.05 wt.% Cu/VWTi catalyst showed stronger K resistance and higher catalytic activity than the commercial VWTi catalyst by reason of its enhanced surface acidity and redox properties [13].

In the presence of 1000 ppm SO₂ at 280 °C, Ce-doped V/WTi showed excellent catalytic activity. An oligomeric V-O-V structure was formed on the catalyst due to the introduction of ceria, facilitating electronic conduction between the vanadia and ceria species, lowering the apparent activation energy and significantly improving the NH₃-SCR reaction performance. The stability of adsorbed NO₂ species was improved, and active vanadium sites were protected from poisoning by the addition of ceria [14]. Ma et al. found that 8 wt.% CeO₂-1 wt.% V₂O₅-WO₃/TiO₂ showed higher than 80% catalytic activity at the temperature range of 190–450 °C, comparable to the performance of 3 wt.% V₂O₅-WO₃/TiO₂, showing that the usage of toxic vanadium oxides can be reduced via ceria doping in the development of low-temperature SCR catalysts [15]. Arfaoui et al. adopted a one-step sol–gel method to synthesize new sulfate and ceria co-modified V₂O₅-TiO₂ nanostructured aerogel catalysts, which presented superior catalytic performance [16]. Hu et al. reported that V-Ce(SO₄)₂/Ti catalysts with abundant reactive acid sites exhibited better activity than the commercial V-W/Ti catalyst and showed a strong tolerance to SO₂ and H₂O [17]. The catalysts 3Ce-V/W/TiO₂ [18], V-5W/Ce/Ti [19], V₀.₈WTiCe₀.₂₅ [20] and V₁Ce₁₀Ti [21] all exhibited excellent SCR activity.

Chi et al. adopted an ultrasonic-assisted impregnation method to prepare Ce-Cu modified V₂O₅/TiO₂ catalysts, exhibiting high NO conversion (>97%) at 200–400 °C [22]. Xu et al. found that among TiO₂-supported vanadium oxide catalysts modified with different amounts of Ce and Sb, V₃Ce₂Sb₂/Ti presented the best SCR performance, over which 90% NO conversion was obtained at 210 °C [23]. The doping of V and Sb into Ce/Ti increased the concentration of Ce⁺⁺, and V/Sb/Ce/Ti exhibited superior catalytic performance and N₂ selectivity (as shown in Figure 2) [24].

The introduction of Mn into VO₂/CeO₂ [110] can speed up the V⁵⁺/V⁴⁺ redox cycle and increase the amount of coordinated NH₃ species and bridging nitrate species during SCR, and therefore improve the deNO₃ activity [25]. Among MoₓV₂O₅-MoO₃-CeO₂/TiO₂ (M = Mn, Cu, Sb, and La) catalysts, Mn₂V₂M₀₃Ceₓ/Ti showed the optimal catalytic activity due to its strong reducibility and abundant acid sites with various strengths, and the tolerance of SO₂ and H₂O were enhanced remarkably by sulfate species formed in the presence of sulfur oxide [26]. V/Mo-Ti presented better NH₃-SCR performance and stronger SO₂ resistance than V/W/Ti catalysts, attributed to the greater abundance of acid sites induced by the introduction of molybdenum, and with increasing Mo⁶⁺ ratio, V/Mo-Ti showed increasing catalytic activity [27]. MoO₃-doped V/WTi exhibited better catalytic performance than V/WTi and 5 wt.% Mo-V/WTi presented the best deNO₃ activity because the introduction of MoO₃ enhanced the amount of surface oxygen species and redox capability and altered the number, type and reaction activities of surface acid sites [28]. The doping of Cr into V/TiO₂ enhanced the low-temperature reductive capacity, increased the amounts of acid sites of weak and medium strength, and promoted the rate of the SCR reaction [29]. The optimal catalytic performance was obtained.
over a 10 wt.% Cr0.2V0.8/TiO2 catalyst. The doping of Nb2O5 into the V/WTi catalyst improved the low-temperature deNOx performance, which was ascribed to the improved dispersion of vanadia and promotion of the reactivity of adsorbed ammonia species [30].

Besides modification with metal oxides, doping with nonmetal elements can also enhance the SCR performance of the catalyst. Marberger et al. found that the doping of 2–4 wt.% SiO2 into V/W/Ti can hamper the growth of anatase crystallites at 600 and 650 °C, resulting in preservation of the low-temperature catalytic activity [31]. Zhao et al. found that the addition of N and S to V2O5/TiO2 can significantly influence NH3-SCR performance, and a catalyst with 3:1:100 (S:N:Ti) molar ratio exhibited superior performance attributed to the large pore volume and surface area, strong reducibility and increased surface acidity, electronic interactions between TiO2 and the dispersed vanadia species, and inhibition of the anatase-to-rutile phase transformation [32,33]. The SCR activity at low temperatures was promoted evidently by the doping of F into V2O5/TiO2 because modification with F promoted the interaction of vanadium species and TiO2 by means of oxygen vacancies with electrons [34]. Liang et al. also found that F-V2O5-WO3/TiO2 could enhance the SCR activity and the resistance to sulfur and water. The surface morphology of the catalyst was eroded and the grain size was reduced by the introduction of an appropriate amount of F [35]. The introduction of a certain amount of phosphorus into V2O5-WO3/TiO2 increased the intrinsic activity for the enhancement of Lewis and Brønsted acid sites on V2O5-WO3/TiO2, and induced the formation of more polymeric surface vanadyl species through spatial effects [36]. Nam et al. added a low content of P into V/Sb/Ce/Ti, and Sb-phosphate and Ce-phosphate instead of VOPO4 were formed, contributing to the enhancement of the redox properties while keeping the acidity almost unchanged, resulting in the promotion of the SCR activity [37]. A heteropoly acid (HPA)-promoted V2O5/TiO2 catalyst presented better catalytic performance and stronger potassium tolerance than WO3-promoted catalysts [38]. The modification of vanadia-based catalysts and their catalytic activity are shown in Table 1.
| Catalysts                  | Preparation Methods | Reaction Conditions                      | NO$_2$ (or NO) Conversion (Temperature Range) | GHSV       | Source |
|---------------------------|---------------------|------------------------------------------|---------------------------------------------|------------|--------|
| Cu-V/TiO$_2$              | Impregnation        | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | >90% (225–375 °C)                          | 26,000 h$^{-1}$ | 10     |
| CuV/WTi                   | Impregnation        | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | >84% (250–400 °C)                          | 10,000 h$^{-1}$ | 11     |
| VWCeCuTi                  | Impregnation        | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | >80% (250–375 °C)                          | 60,000 h$^{-1}$ | 13     |
| V/Ce/WTi                  | Precipitation       | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$, 5vol% H$_2$O | 95% (250–450 °C)                          | 18,000 h$^{-1}$ | 14     |
| VCeTiSO$_4^{2-}$          | Sol–gel             | 0.1% NO, 0.1% NH$_3$, 8 vol% O$_2$, 3.5vol%H$_2$O | >80% (275–450 °C)                          | 120,000 h$^{-1}$ | 16     |
| V-Ce(SO$_4$)$_2$/Ti        | Impregnation        | 0.08% NO, 0.08% NH$_3$, 5 vol% O$_2$, 0.05%S$_2$O$_5$, 5vol%H$_2$O | 100% (300–450 °C)                          | 150,000 mL/g·h | 17     |
| V$_5$CeSb$_2$/TiO$_2$      | Impregnation        | 0.1% NO, 0.1% NH$_3$, 3 vol% O$_2$      | >97% (200–400 °C)                          | 45,000 h$^{-1}$ | 22     |
| V–Mn/Ce                   | Hydrothermal        | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | >80% (200–350 °C)                          | 160,000 h$^{-1}$ | 25     |
| V3Mo5/WTi                 | Impregnation        | 0.05% NO, 0.05% NH$_3$, 3 vol% O$_2$     | >80% (200–300 °C)                          | 60,000 h$^{-1}$ | 28     |
| 10%Cr$_{0.2}$V$_{0.8}$/TiO$_2$ | Impregnation     | 0.05% NO, 0.05% NH$_3$, 3 vol% O$_2$     | >85% (160–280 °C)                          | 60,000 mL/g·h | 29     |
| 6%Nb–3%V/W–Ti             | Impregnation        | 0.05% NO, 0.05% NH$_3$, 3 vol% O$_2$     | >90% (225–400 °C)                          | 60,000 h$^{-1}$ | 30     |
| 4%Si$_2$V/10%W/Ti         | Co-impregnation     | 0.05% NO, 0.06% NH$_3$, 10 vol% O$_2$    | >80% (300–500 °C)                          | 50,000 h$^{-1}$ | 31     |
| S$_3$N$_1$V/Ti$_{100}$    | Sol–gel             | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | 100% (240–450 °C)                          | 27,549 h$^{-1}$ | 32     |
| VTF–(NH$_4$)$_2$TiF$_6$    | Sol–gel             | 0.05% NO, 0.06% NH$_3$, 5 vol% O$_2$     | 78.5% (240 °C)                             | 38,900 h$^{-1}$ | 34     |
| 0.2%F–VW/Ti               | Impregnation        | 0.07% NO, 0.07% NH$_3$, 5 vol% O$_2$     | >95% (160–360 °C)                          | 30,000 h$^{-1}$ | 35     |
| 1P–VWTi                   | Impregnation        | 0.05% NO, 0.05% NH$_3$, 5 vol% O$_2$     | 96% (250 °C)                               | 70,000 h$^{-1}$ | 36     |
| 5%V/15%TPA/Ti             | Impregnation        | 0.1% NO, 0.1% NH$_3$, 4 vol% O$_2$, 2.3 vol% H$_2$O | 100% (300 °C)                             | 180,000 h$^{-1}$ | 38     |
The improvements in low-temperature performance accomplished via modification with metal oxides or nonmetal elements were mainly related to modulation of the redox capability and acidity of the vanadia-based catalysts. Besides doping with active components, the catalyst supports were also modified to further improve the deNO\textsubscript{x} activity.

2.2. The Effect of Different Supports

TiO\textsubscript{2} has been applied as a support for commercial vanadia-based catalysts for decades due to its favorable properties, including good surface dispersion of V species on TiO\textsubscript{2} in comparison with other supports (Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, et al.) as well as weak and reversible sulfation under SCR reaction conditions [8,39,40]. However, at high reaction temperatures, anatase TiO\textsubscript{2} will transform to rutile TiO\textsubscript{2}, which leads to catalyst sintering accompanied by decreases in the surface area and activity [41]. Recently, many attempts have been made to improve vanadia-based catalysts by modifying the TiO\textsubscript{2} support or using diverse support materials.

Vanadium oxides dispersed on microporous TiO\textsubscript{2} supports produced much less N\textsubscript{2}O than commercial TiO\textsubscript{2}-supported catalysts during the process of NH\textsubscript{3}-SCR reaction, because the formation of bulk-like V\textsubscript{2}O\textsubscript{5} species, which resulted in the formation of N\textsubscript{2}O, was suppressed (as shown in Figure 3) [42]. The pore structure of TiO\textsubscript{2} determined the types of vanadium species present, which affected the sulfur resistance during the SCR reaction. A 5 wt.% V/Ti (microporous TiO\textsubscript{2}) showed stronger resistance to sulfur poisoning and better activity than a 5 wt.% V/Ti (mesopore DT-51) having bulk-like VO\textsubscript{x} species [43]. A catalyst with 5 wt.% vanadia ultrasonically impregnated on a TiO\textsubscript{2} support with a large surface area (380.5 m\textsuperscript{2}/g) had a 100 °C wider operating temperature window and higher N\textsubscript{2} selectivity than the traditional vanadia-based catalyst due to enhanced redox capability and total acidity [44]. Ti-bearing blast furnace slag was used to prepare the TiO\textsubscript{2}-SiO\textsubscript{2} support, which was then used to support V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3} and the catalyst presented enhanced acidity and redox ability for active species and promoted the SCR activity compared with a catalyst using commercial TiO\textsubscript{2} as support [45]. Mixed tungsten--titanium-pillared clays were used to support vanadium oxides, and the synthesized catalysts showed a uniform distribution of WTi-pillars between the clay layers and showed good catalytic performance in NH\textsubscript{3}-SCR [46]. Catalysts on other novel supports were also investigated, such as V\textsubscript{2}O\textsubscript{5} supported on reduced TiO\textsubscript{2} [47], vanadium impregnated on silica-pillared layered titanate (SiO\textsubscript{2}-Ti\textsubscript{4}O\textsubscript{9}) [48], supported vanadium-substituted Keggin polyoxometalates (POM) [49], V\textsubscript{2}O\textsubscript{5}/H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}-nanotubes and V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}-nanotubes [50], 1V4Ce/Ti-PILC (1 wt.% V and 4 wt.% Ce) [51], and V/Co\textsubscript{1-x}Ti\textsubscript{x} (x = 0.3, 0.5) [52].

![Figure 3](image_url)  
Figure 3. NO\textsubscript{x} conversion and N\textsubscript{2}O formation during SCR of NO with NH\textsubscript{3} over VO\textsubscript{x}/DT-51 and VO\textsubscript{x}/MP-TiO\textsubscript{2} calcined at various temperatures. Measurement was performed after reaching steady state in wet conditions at 400 °C [42]. Reproduced with permission from [42], copyright 2018, Elsevier.

Ce-based supports for vanadium oxide NH\textsubscript{3}-SCR catalysts have also attracted interest. In our previous study, the homogeneous precipitation method was used to prepare vanadium oxides/CeO\textsubscript{2} catalysts, and the catalyst exhibited high NO\textsubscript{x} conversion and strong tolerance to SO\textsubscript{2} and H\textsubscript{2}O [53].
Incorporating Ti into V2O5/CeO2 improved the NOx conversion, N2 selectivity and resistance to SO2 and H2O due to the lower crystallinity, more abundant acid sites, better dispersion of surface V species and greater number of reduced species [54]. Modification of VO2/CeO2 with NbO2 promoted the redox capability and acidity, leading to better NH3-SCR activity and stronger tolerance to SO2/H2O than the unmodified VO2/CeO2 catalyst; and 30Nb-1VOx/CeO2 exhibited better NH3-SCR performance than 3V2O5-10WO3/TiO2 (as shown in Figure 4) [55,56].

ZrO2 supports with various morphologies (mesoporous, rod, star, sphere, hollow) were loaded with vanadium oxide, and 3 wt.% V/Zr (mesoporous) exhibited a wide operating temperature window and excellent N2 selectivity. The content of tetravalent vanadium ions on the surface of the catalyst and catalytic performance decreased in the order of mesoporous > hollow spheres > stars > rods [57]. In addition, there are several reports on the use of Zr-modified supports such as in 5wt.%V/Zr0.3Ce0.7 [58], V/ZrCe0.6 [59], Co-V/Zr-Ce [60], which enhanced the SCR performance of the vanadia-based catalysts. A catalyst with vanadium–tungsten oxides supported on CuCeOx microflowers showed excellent deNOx performance at low temperatures, attributed to the facile electron transfer among V, Cu and Ce ions, decreasing the apparent activation energy of the NH3-SCR reaction (Ea = 16.59 kJ/mol) [61]. A V/Ce0.9Fe0.1 solid solution also presented relatively high SCR activity at low temperature (below 300 °C) [62].

Carbon materials, including carbon nanotubes (CNT), carbon fibers (ACF) and activated carbon (AC), can also be used to support vanadia-based catalysts for NH3-SCR for large specific surface area and pore volume. Carbon nanotube-supported vanadium oxide (V2O5/CNT) exhibited high NO reduction activity and high stability at low-temperatures, and the activity in the presence of sulfur dioxides was significantly promoted [63]. Sulfur dioxide could enhance the catalytic activity of a V2O5/SiC catalyst at 250 °C because pre-adsorption with SO2 + O2 enhanced NH3 adsorption and at low temperatures, NO could effectively react with the ammonium bisulfate that was formed on the surface of the catalyst [64]. Excellent SCR performance and SO2 resistance were also achieved by 3 wt.%Fe-0.5 wt.%V/AC [65], and Mn-Ce-V/AC [66].

Improving the properties of the support could thus improve the dispersion of vanadium species and the interaction between the support and active components, enhance electron transfer between active components, enlarge the specific surface area, and strengthen the redox capability and acidity, all of which are beneficial to accelerating the SCR reaction.

Figure 4. NH3-SCR activity over VOx/CeO2 and V2O5-WO3/TiO2 catalysts [55]. Reproduced from [55], copyright 2018, Royal Society of Chemistry.
2.3. The Effect of Preparation Method

The preparation methods utilized for catalysts mainly include the precipitation method, sol–gel method, hydrothermal method, impregnation method, and other specialized synthesis methods. Different synthesis methods and synthesis parameters influence the nanostructures, morphologies, and surface physicochemical properties, finally affecting the NH$_3$-SCR catalytic activity. Hence, it is important to optimize the synthesis method to improve the NH$_3$-SCR activity over vanadia-based catalysts.

Compared to materials prepared by incipient wetness impregnation, coprecipitated V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts presented superior SCR performance derived from their increased ammonia adsorption capacity due to the existence of new surface WO$_x$ site-associated surface defects on the TiO$_2$ support [67]. A V/Ce/WTi-DP (deposition precipitation) catalyst exhibited more O$_\alpha$, stronger reducibility and more surface Ce species, thus showing less N$_2$O formation and better medium-temperature NH$_3$-SCR performance than similar catalysts prepared by impregnation [68]. CeO$_2$-modified V$_2$O$_5$/TiO$_2$ synthesized via chemical vapor condensation exhibited a higher ratio of Ce$^{3+}$ and showed higher reducibility and acidity than that synthesized by the impregnation method [69]. In our previous work, VO$_x$/CeO$_2$ synthesized via the homogeneous precipitation method presented better catalytic performance and stronger tolerance to H$_2$O and SO$_2$ than that synthesized via sol–gel method, incipient wetness impregnation and rotary evaporation impregnation, which can be ascribed to the lower crystallinity of CeO$_2$ on the surface, greater abundance of acid sites and vanadium species, and better dispersion of V species [53]. The support synthesis methods had an effect on structure and performance of VO$_x$/CeO$_2$ catalysts, and the catalyst from precipitation method prepared-support was more active than that from citrate method due to higher surface area and a more effective incorporation of V sites into the support surface [70]. A series of VWTi nanoparticle catalysts were directly synthesized via the sol–gel method, and V$_{0.02}$W$_{0.04}$Ti showed the best SCR activity and the lowest apparent activation energy due to a high concentration of distorted and reducible vanadium species [71].

Besides these conventional synthesis methods, several novel preparation methods were developed to enhance catalytic activity of vanadia-based NH$_3$-SCR catalysts. Chen et al. prepared V$_{0.1}$Ti$_{0.9}$O$_{2.5}$ catalysts by flame synthesis with promoted low-temperature activity due to strong redox properties, and different synthesis conditions also affected the properties of the catalysts and their catalytic activity [72]. Arfaoui prepared a V$_2$O$_5$-CeO$_2$-TiO$_2$-SO$_4^{2-}$ nanostructured aerogel catalyst via a one-step sol–gel method accompanied by the supercritical drying process, which presented a large surface area (66 m$^2$/g), large porosity and good thermal stability [16]. Tuning the interaction degree supplied by external forces can regulate the morphology. Rotation-assisted hydrothermal synthesis can be used to prepare thick multiwalled titanate nanotubes and when used as the support for vanadium–tungsten-oxide, the resulting catalysts presented stable catalytic activity because the sintering of VO$_x$ was suppressed by the multiwalled nanotubes [73]. Doronkin et al. found that V/Ti and V-W/Ti catalysts prepared via incipient wetness impregnation and grafting with highly dispersed, isolated and polymeric V-oxo species exhibited high SCR activity [74].

In the synthesis of catalysts, different preparation parameters can also affect the physicochemical properties and the catalytic activity. For example, different vanadium precursors have an influence on the dispersion of V species and catalytic performance [75]. V$_2$O$_5$/TNTs catalysts prepared using VOSO$_4$ as the V precursor exhibited stronger synergistic effects with the TNTs than those made with an NH$_4$VO$_3$ precursor, and active metal precursors containing cation groups were superior to those with anion groups (as shown in Figure 5) [76]. During the preparation process of iron vanadate, the pH value determined the stoichiometry of the FeVO$_4$/TiO$_2$-WO$_3$-SiO$_2$ product: vanadium-rich samples were prepared at pH lower than 6, stoichiometric FeVO$_4$ was obtained in the pH range of 4–6, while samples prepared at pH > 6 were rich in Fe$_2$O$_3$ [77]. The NH$_3$ adsorption capacity of Ce-doped V$_2$O$_5$-WO$_3$/TiO$_2$ was affected by the sequence of impregnation by Ce and W, and 0.2V-5W-5Ce/Ti exhibited stronger SO$_2$ and H$_2$O tolerance than 0.2V-(5Ce5W)/Ti and 0.2V-5Ce-5W/Ti [78]. Compared to the untreated
sample, V-Ce-Ni/TiO₂ catalysts treated by nonthermal plasma possessed smaller particle size, better dispersion and more uniform distribution of active sites, as well as larger number of oxygen vacancy and acid sites. Therefore, the plasma-treated catalysts showed improved catalytic performance at low temperatures with a wider operating temperature window [79]. Moreover, the treatment atmosphere can also have an influence on catalytic performance. The ratios of active polymeric V-O-V species and further NH₃-SCR activity decreased in the following order: V/Ti > V/Ti-O₂ > V/Ti-N₂ > V/Ti-NH₃ [80].

Uniformly active phase loaded SCR catalyst (V₂O₅/TNTs) synthesized via ion-exchange mechanism: achieving excellent NOₓ removal efficiency and alkali resistance.

Figure 5. SCR catalysts (V₂O₅/TNTs) uniformly loaded with active phase synthesized via ion-exchange mechanism [76]. Reproduced with permission from [76], copyright 2018, Elsevier.

2.4. Metal Vanadates

Although vanadia-based catalysts show superior catalytic performance at medium temperatures and have been widely applied in the deNOₓ process, the volatility and the toxicity of vanadium oxide at high temperature is a crucial problem. However, metal vanadates present better thermal stability than V₂O₅ due to their higher melting points (e.g., 780, 850, 1030 and 1100 °C for copper vanadate, iron vanadate, manganese vanadate and cerium vanadate, respectively). Therefore, metal vanadates can be candidates for vanadia-based catalysts with great potential [81].

Iron vanadates (FeVO₄) have recently been extensively studied as active NH₃-SCR catalysts. Abundant surface defects existed on a FeVO₄/TiO₂ catalyst for the adsorption and activation of reactants, and the true active sites were FeVO₄ phase surface-enriched with VO₂⁺ species. Thus, similar to V₂O₅/TiO₂, FeVO₄/TiO₂ showed superior catalytic performance and H₂O/SO₂ tolerance [1]. Fe₀.₇₅V₀.₂₅O₅ exhibited excellent SCR performance in the temperature range of 175–400 °C. It was found that the formation of amorphous FeVO₄ resulted from the incorporation of V into Fe₂O₃, and the apparent activation energy decreased due to the synergistic effect of FeVO₄ and Fe₂O₃ improving the catalytic activity at low temperatures [82]. Due to the greater electronic inductive effect, Fe₂V₄O₁₃/TiO₂ showed stronger redox capability and more sites accessible to NOₓ/NH₃ than FeVO₄/TiO₂ and thus presented higher activity in the presence of H₂O [83].

Marberger et al. found that compared to the 2.3 wt.% V₂O₅/TiO₂-WO₃-SiO₂ catalyst, 4.5 wt.% FeVO₄/TiO₂-WO₃-SiO₂ showed enhanced catalytic performance, and the decomposition of FeVO₄ led to an activation effect due to the dispersal and migration of VO₂⁺ species to the surface of the support material, which were the active species responsible for NH₃-SCR [84]. Wu et al. proposed that the performance of FeVO₄/TiO₂-WO₃-SiO₂ was structure-sensitive, and that the pH values adopted during the preparation process had an influence on the nanostructure and morphology. The optimal catalyst showed 90% NOₓ conversion in the temperature range of 246–476 °C and strong tolerance to SO₂ and
H₂O [85]. The doping of Er into FeVO₄/TiWSi could block the transformation to rutile, inhibiting the deactivation of FeVO₄ due to thermal aging and thus improving the activity after thermal treatment, and the Fe loading determined the medium/low-temperature catalytic activity. Fe₀.₅Er₀.₅VO₄ was found to exhibit superior catalytic performance and stability [86].

The oxidation of NO to NO₂ was enhanced by the coexistence of Ce⁴⁺ species stabilized as CeO₂ with bulk CeVO₄. Aging treatments under wet atmosphere at 500 and 600 °C did not result in the sublimation and loss of vanadium [87]. The introduction of Zr into CeVO₄ to form a Ce₁₋ₓZrₓVO₄ solid solution led to high activity, with a 125 °C light-off temperature and a wide temperature window of 150–375 °C by reason of the increased surface area, surface active oxygen species and acid sites of the catalysts [81]. Zr-CeVO₄/TiO₂-nanosheets showed better SCR performance, stability and tolerance to H₂O/SO₂ than nanoparticles due to their more abundant Brønsted acid sites and active oxygen species [88]. A catalyst with Ce:V = 1:1 supported on sulfated zirconia showed high activity in the presence of SO₂ and potassium. The incorporation of vanadium led to the formation of CeVO₄, preventing reaction between SO₂ and CeO₂ and maintaining the reactivity of active sites, thus enhancing the tolerance toward SO₂ [89]. The doping of Sn into CeVO₄ catalysts can broaden the temperature window and improve the resistance to SO₂ and H₂O, mainly resulting from the large specific surface area (from 40.75 to 49.05 m²/g), strong interactions among vanadium, cerium and tin, and large numbers of oxygen vacancies and acid sites [90].

Compared to CuV₂O₆ (Cu₁/Ti), Cu₂V₂O₇ (Cu₂/Ti), and Cu₃V₂O₈ (Cu₃/Ti), Cu₅V₂O₁₀ (Cu₅/Ti) presented optimal redox behavior and the largest number of acid sites, and therefore presented the greatest SCR performance at low temperatures [91]. The addition of Sb as a promoter can further improve the SCR activity over copper vanadate catalysts due to the improved redox properties [91]. SO₂ and O₂ can be used to modify Sb-promoted Cu₃V₂O₈ on TiO₂, and 400 °C was an adequate functionalization temperature to promote the redox behavior and increase the number of Bronsted acid sites, resulting from the more abundant surface Cu(SO₄) or from a proper combination of the metal-bound SO₄²⁻ species with monodentate and bidentate binding configurations, to enhance the catalytic performance (as shown in Figure 6) [92].

Figure 6. Schematic representation of Cu₃-Sb₁.₄/TiO₂ surface prior to and post SO₄²⁻ functionalization. (a) Change in the surface species upon SO₄²⁻ functionalization to potentially dissociate the Cu₃V₂O₈ particles and generate V, Cu, or Sb-based sulfite or sulfate species. (b) Covalent or ionic characters of the S-O bonds possibly inherent to the metal-SO₄²⁻ species [92]. Reproduced with permission from [92], copyright 2019, Elsevier.
In summary, metal vanadates can not only increase the low/medium-temperature NH$_3$-SCR activity but also enhance the thermal stability [93,94]. The metal vanadates have aroused the interest of researchers due to their excellent chemical and physical properties. In future studies, the metal vanadate can obtain higher SCR activity through doping different elements or changing the preparation methods, etc.

2.5. Specific Structures

Tuning the structure and morphology of nanoparticle catalysts can enhance the NH$_3$-SCR activity. Thus, researchers have made great efforts to regulate the structure and morphology of vanadia-based catalysts. A FeVO$_4$ nanorod/TiO$_2$ monolith catalyst exhibited a remarkably higher catalytic activity than a traditional FeVO$_4$ nanoparticle/TiO$_2$ catalyst, due to the predominantly exposed reactive planes (−210) contributing to the stronger redox capability and more abundant surface active oxygen species [95]. Multichannel TiO$_2$ nanotubes can provide abundant surface-adsorbed oxygen species and anchor active components efficiently, and a CeVTi-nanotube catalyst presented satisfactory NH$_3$-SCR activity in the temperature range of 220–460 °C [96]. Bulk TiO$_2$ was treated by a hydrothermal reaction to obtain zeolitic microporous TiO$_2$ to support vanadia-based catalysts, and compared to conventional V$_2$O$_5$/TiO$_2$, the catalyst not only maintained excellent SCR performance but also suppressed N$_2$O emission significantly [97]. V/CeO$_2$ nanopolyhedrons showed better SCR activity than nanocubes and nanorods for their abundant surface acid sites and appropriate redox ability (as shown in Figure 7) [98]. TiO$_2$ with different crystal types was used to support 3 wt.%V$_2$O$_5$, and the catalytic activity was found to depend on the dominant crystal facets of the TiO$_2$ nanoparticles. V$_2$O$_5$ loaded onto sheet-like TiO$_2$, on which anatase (001) facets were preferentially exposed, presented a better catalytic performance than that loaded onto commercial TiO$_2$ (TiO$_2$-P25) or octahedral TiO$_2$ with preferentially exposed anatase (101) facets, as the catalyst presented larger amounts of chemisorbed oxygen and better dispersion and stronger reducibility of V species [99]. A titania nanotube-encapsulated vanadium oxide catalyst exhibited a monolayer of isolated species where V$^{5+}$ was the dominant oxidation state and demonstrated a wide operating temperature window, which was due to the active species being well dispersed on the support surface [100].

![Figure 7. NO conversion as a function of temperature in the NH$_3$-SCR reaction [98]. Reproduced with permission from [98], copyright 2018, Elsevier.](image-url)
3. Reaction Mechanism at Low Temperatures

Although vanadia-based NH$_3$-SCR catalysts have been commercialized for decades, the reaction mechanism on the catalysts has still been a focus of research in recent years, including the identification of active sites and intermediates and elucidation of the interaction of the active sites with the reactants. The NH$_3$-SCR reaction pathway proceeds as follows: the adsorbed NH$_3$ species react either with adsorbed nitrates/nitrites (Langmuir–Hinshelwood mechanism, i.e., L–H) or directly with gaseous NO (Eley–Rideal mechanism, i.e., E–R) to generate intermediates that subsequently decompose to N$_2$ and H$_2$O [5,101,102]. The acid sites and redox sites work together in the NH$_3$-SCR reaction on the catalysts, and the close coupling of acid and redox sites is a design principle for SCR catalysts with excellent NOx purification efficiency [103].

In a debating issue about the active sites of NH$_3$-SCR on VWTi catalysts, it has been reported before that both surface NH$_4^+$ and NH$_3$ participated in the NH$_3$-SCR reaction and the coverage of surface tungsten and vanadia oxide species, moisture, and temperature determined their relative population [104]. The large amount of surface NH$_4^+$ intermediates present a lower specific SCR activity (TOF) than the minority surface NH$_3$ intermediates. The SCR reaction rate does not depend on the exposed Ti$^{4+}$ sites on the support. Marberger et al. [105] proposed that NO reacts predominantly with coordinated NH$_3$ adsorbed on Lewis acid sites consisting of isolated V$^{5+}$ which were reduced only in the coexistence of NH$_3$ and NO, and the reduction of V$^{5+}$ was accompanied by the formation of a nitrosamide intermediate at low temperature. Brønsted acid sites, serving as an NH$_3$ pool and hardly contributing to the NH$_3$-SCR reaction, can replenish the Lewis acid sites. The rate-determining step is re-oxidation and regeneration of active Lewis acid sites.

The presence of H$_2$O and changes in the redox state of vanadia-based catalysts led to a reversible change between Brønsted and Lewis acid sites. Under reducing conditions, the surface was enriched with Lewis acid sites because that ammonia could be coordinated on the reduced vanadium sites as supplementary of Lewis acid sites, while more abundant Brønsted acid sites on the V/Ti catalyst surface were generated under an oxidizing environment [106]. Brønsted acid sites are important at low temperatures, while Lewis acid sites dominate the overall reaction at high temperatures. Lewis acid sites can transform to Brønsted acid sites at temperatures above 300 °C through hydrogen migration [107]. The number of Lewis acid sites decreased and the amount of Brønsted acid sites increased with changes in the vanadium content. The increase of vanadium pentoxide loading resulted in the increase of the amount of V-OH in polymeric vanadyl and the decrease of the amount of isolated vanadyl (V=O) species [108].

Most current investigations of the NH$_3$-SCR reaction process over V-based catalysts have mainly concentrated on isolated monomeric vanadyl species, while the polymerization of vanadium species and the coupling effects were not taken into consideration. In our previous study [109], DFT calculations were carried out to elucidate the differences between the NH$_3$-SCR mechanisms taking place on polymeric and monomeric vanadyl species at atomic scale. The results showed that NH$_3$ adsorbed on surface Ti sites transferred a hydrogen atom to the vanadyl species firstly and then reacted with gaseous NO according to the Eley–Rideal mechanism. An NH$_2$NO intermediate and a V=OH or V-OH$_2$ group were formed and then N$_2$ and H$_2$O were generated from the decomposition of NH$_2$NO. The consumed surface oxygen on the vanadyl species was replenished by gas-phase O$_2$. The catalytic cycle was completed when V=O groups were regenerated (as shown in Figure 8).

For the monomeric vanadyl species, a VOOH intermediate was formed after the transfer of an H atom of the adsorbed NH$_3$ to the adsorbed O$_2$ on vanadyl species and rapidly transformed into O=V=OH. However, for polymeric vanadyl species, the thermal stability and lifetime of the VOOH intermediate were enhanced because a hydrogen bond was formed between VOOH and the adjacent V=O group. Therefore, on polymeric vanadyl species, the VOOH intermediate can easily react with NO. The overall reaction barrier of the catalytic cycle decreases and the reaction pathway for the regeneration of redox sites is shortened due to the coupling effect of polymeric vanadyl species. Therefore, the NH$_3$-SCR reaction rate is significantly enhanced on polymeric species.
Figure 8. Mechanism of the standard NH3-SCR reaction. (A) Reactions over monomeric vanadia/TiO2 surfaces. (B) Reactions over dimeric vanadia/TiO2 surfaces. Reactants are marked in red, and products are marked in blue [109]. Reproduced from [109], copyright 2018, American Association for the Advancement of Science.

Jaegers et al. clarified that the formation of oligomeric vanadia structures on supported V2O5-WO3/TiO2 was promoted by the unreactive surface tungsten oxide (WO3), revealing a 2-site mechanism due to the presence of a proportional relationship of SCR reaction rate to the square of surface VOx concentration. The enhancement of the NH3-SCR reaction from the incorporation of a promoter occurs via a structural effect generated by adjacent surface sites rather than an electronic effect [110].

The presence of H2O can have an influence on the reaction pathway for NH3-SCR at low temperatures. In the standard and fast SCR reactions, adsorbed NH3 reacts with nitrite species to generate N2 and H2O (nitrite path), while the reaction between gaseous NO and NH4NO3 formed from adsorbed ammonia species and surface nitrates to emit NO2, H2O and N2 (NH4NO3 path) does not occur at low temperatures without H2O, and in the presence of H2O both the “nitrite path” and the “NH4NO3 path” contribute to the NH3-SCR reaction [111].

For vanadia-based catalysts, different NH3-SCR reaction pathways occur on various vanadium species. The reaction mechanism can be more complicated over modified vanadia-based catalysts and is also related to the concentration of vanadium oxide and the reaction temperature. Therefore, a variety of modern characterization and computational techniques should be applied in order to have a better view of the NH3-SCR reaction mechanism, guiding the design of excellent deNOx catalysts.

4. Conclusions and Perspective

Commercial V2O5-WO3/TiO2 catalysts have been widely applied for abating nitrogen oxides from mobile and stationary sources. However, the poor low-temperature activity of vanadia-based catalysts restricts their broader application in the process of NOx purification. Therefore, this review summarizes the latest research progress on the improvement of deNOx performance over vanadia-based catalysts at low temperatures and the NH3-SCR reaction mechanism, and outlines opportunities and challenges for vanadia-based catalysts in the near future.

The NH3-SCR catalytic performance over vanadia-based catalysts at low temperatures is mainly determined by polymeric vanadyl species, while monomeric species presented lower catalytic activity. The NH3-SCR reaction needs acid sites and redox sites to work together. The good dispersion of sites with the same function and close coupling of sites with different functions are crucial for the design of excellent NH3-SCR catalysts. However, considering the complexity of the SCR reaction, the NH3-SCR reaction mechanisms and the structure–activity relationships still need to be investigated in-depth to gain an enhanced understanding and thus improve catalyst design theory. Furthermore, due to the
The utilization of di... elements can improve the low-temperature SCR activity effectively. Diverse supports have been used to improve the dispersion of vanadium oxide and the interaction between the supports and the active components. The utilization of different preparation methods and use of metal vanadates and specific structures can also promote the catalytic performance of vanadia-based catalysts at low temperatures. Though great progress has been made recently, the catalysts still face many challenges in practical application, such as alkali poisoning and halogen poisoning. We need to develop catalysts with better performance to deal with the practical problems with superior low-temperature activity, wide operation windows, strong mechanical and thermal stability, and excellent resistance to alkali, heavy-metal, SO₂, and P/HCl poisoning. However, due to the volatility and toxicity of vanadium oxide, in the future catalysts with a low loading of vanadium or even no vanadium may be the main development trend in the field of NOx removal.

**Funding:** This work was supported by the National Natural Science Foundation of China (21637005 and 51822811) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA23010201).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Liu, F.; He, H.; Lian, Z.; Shan, W.; Xie, L.; Asakura, K.; Yang, W.; Deng, H. Highly dispersed iron vanadate catalyst supported on TiO₂ for the selective catalytic reduction of NOₓ with NH₃. *J. Catal.* **2013**, *307*, 340–351. [CrossRef]

2. Baiker, A.; Dollenmeier, P.; Glinski, M.; Reller, A. Selective catalytic reduction of nitric oxide with ammonia: II. Monolayers of vanadia immobilized on titania-silica mixed gels. *Appl. Catal.* **1987**, *35*, 365–380. [CrossRef]

3. Baiker, A.; Dollenmeier, P.; Glinski, M.; Reller, A. Selective catalytic reduction of nitric oxide with ammonia: I. Monolayer and multilayers of vanadia supported on titania. *Appl. Catal.* **1987**, *35*, 351–364. [CrossRef]

4. Rosenberg, H.S.; Curran, L.M.; Slack, A.V.; Ando, J.; Oxley, J.H. J.P.; Science, C. Post combustion methods for control of NOx emissions. *Prog. Energy Combust. Sci.* **1980**, *6*, 287–302. [CrossRef]

5. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NOₓ by ammonia over oxide catalysts: A review. *Appl. Catal. B* **1998**, *18*, 1–36. [CrossRef]

6. Lai, J.K.; Wachs, I.E. A perspective on the selective catalytic reduction (SCR) of NO with NH₃ by supported V₂O₅-WO₃/TiO₂ catalysts. *ACS Catal.* **2018**, *8*, 6537–6551. [CrossRef]

7. Han, L.; Cai, S.; Gao, M.; Hasegawa, J.Y.; Wang, P.; Zhang, J.; Shi, L.; Zhang, D. Selective catalytic reduction of NOₓ with NH₃ by using novel catalysts: State of the art and future prospects. *Chem. Rev.* **2019**, *119*, 10916–10976. [CrossRef]

8. Xu, J.; Chen, G.; Guo, F.; Xie, J. Development of wide-temperature vanadium-based catalysts for selective catalytic reducing of NOₓ with ammonia: Review. *Chem. Eng. J.* **2018**, *333*, 507–518. [CrossRef]

9. Kobayashi, M.; Kuma, R.; Masaki, S.; Sugishima, N. TiO₂-SiO₂ and V₂O₅/TiO₂-SiO₂ catalyst: Physico-chemical characteristics and catalytic behavior in selective catalytic reduction of NO by NH₃. *Appl. Catal. B* **2005**, *50*, 173–179. [CrossRef]

10. Zhao, X.; Huang, L.; Li, H.; Hu, H.; Han, J.; Shi, L.; Zhang, D. Highly dispersed V₂O₅/TiO₂ modified with transition metals (Cu, Fe, Mn, Co) as efficient catalysts for the selective reduction of NO with NH₃. *Chin. J. Catal.* **2015**, *36*, 1886–1899. [CrossRef]

11. Shen, M.; Li, C.; Wang, J.; Xu, L.; Wang, W.; Wang, J. New insight into the promotion effect of Cu doped V₂O₅/GeO₂-TiO₂ for low temperature NH₃-SCR performance. *RSC Adv.* **2015**, *5*, 35155–35165. [CrossRef]

12. Wang, H.; Wang, B.; Zhou, J.; Li, G.; Zhang, D.; Ma, Z.; Xiong, R.; Sun, Q.; Xu, W.Q. CuO modified vanadium-based SCR catalysts for Hg⁰ oxidation and NO reduction. *J. Environ. Manag.* **2019**, *239*, 17–22. [CrossRef] [PubMed]

13. Li, H.; Miao, J.; Su, Q.; Yu, Y.; Chen, Y.; Chen, J.; Wang, J. Improvement in alkali metal resistance of commercial V₂O₅-WO₃/TiO₂ SCR catalysts modified by Ce and Cu. *J. Mater. Sci.* **2019**, *54*, 14707–14719. [CrossRef]
14. Li, C.; Shen, M.; Wang, J.; Wang, J.; Zhai, Y. New insights into the promotional mechanism of ceria for activity and ammonium bisulfate resistance over V/W/ Ti catalyst for selective catalytic reduction of NO with NH3. Appl. Catal. A 2018, 560, 153–164. [CrossRef]
15. Ma, Z.; Wu, X.; Feng, Y.; Si, Z.; Weng, D.; Shi, L. Low-temperature SCR activity and SO2 deactivation mechanism of Ce-modified V2O5-WO3/TiO2 catalyst. Prog. Nat. Sci. Mater. Int. 2015, 25, 342–352. [CrossRef]
16. Arfaoui, J.; Ghorbel, A.; Petitto, C.; Delahay, G. Novel V2O5-CeO2-TiO2-SO42− nanostructured aerogel catalyst for the low temperature selective catalytic reduction of NO by NH3 in excess O2. Appl. Catal. B 2018, 224, 264–275. [CrossRef]
17. Hu, W.; Zhang, Y.; Liu, S.; Zheng, C.; Gao, X.; Nova, I.; Tronconi, E. Improvement in activity and alkali resistance of a novel V-Ce(SO4)2/Ti catalyst for selective catalytic reduction of NO with NH3. Appl. Catal. B 2017, 206, 449–460. [CrossRef]
18. Li, C.; Shen, M.; Wang, J.; Wang, J.; Zhai, Y. New insights into the role of WO3 on the enhanced performance and SO2 deactivation of NO with NH3. Appl. Catal. A 2018, 560, 153–164. [CrossRef]

19. Li, C.; Shen, M.; Wang, J.; Wang, J.; Zhai, Y. New insights into the role of WO3 on the enhanced performance and SO2 deactivation of NO with NH3. Appl. Catal. A 2018, 560, 153–164. [CrossRef]
20. Zhao, W.; Dou, S.; Zhang, K.; Wu, L.; Wang, Q.; Shang, D.; Zhong, Q. Promotion effect of S and N co-addition on the catalytic performance of V2O5/TiO2 for NH3-SCR of NOx. Chem. Eng. J. 2019, 364, 401–409. [CrossRef]
21. Zhao, W.; Zhong, Q.; Pan, Y.; Zhong, Q. Promotion effect of S and N co-addition on the catalytic performance of V2O5/TiO2 for NH3-SCR of NOx. Chem. Eng. J. 2019, 364, 401–409. [CrossRef]
22. Marberger, A.; Ferri, D.; Rentsch, D.; Krumbeich, F.; Elsener, M.; Krocher, O. Effect of SiO2 on co-impregnated V2O5/WO3/TiO2 catalysts for the selective catalytic reduction of NO with NH3. Catal. Today 2019, 320, 123–132. [CrossRef]
23. Zhao, W.; Dou, S.; Zhang, K.; Wu, L.; Wang, Q.; Shang, D.; Zhong, Q. Promotion effect of S and N co-addition on the catalytic performance of V2O5/TiO2 for NH3-SCR of NOx. Chem. Eng. J. 2019, 364, 401–409. [CrossRef]
24. Zhang, S.; Zhong, Q.; Zhao, W.; Li, Y. Surface characterization studies on F-doped V2O5/TiO2 catalyst for NO reduction with NH3 at low-temperature. Chem. Eng. J. 2014, 253, 207–216. [CrossRef]
25. Liang, Q.; Li, J.; He, H.; Yue, T.; Tong, L. Effects of SO2 and H2O on low-temperature NO conversion over F-V2O5-WO3/TiO2 catalysts. J. Environ. Sci. 2020, 90, 253–261. [CrossRef] [PubMed]
36. Yan, T.; Liu, Q.; Wang, S.; Xu, G.; Wu, M.; Chen, J.; Li, J. Promoter rather than inhibitor: Phosphorus incorporation accelerates the activity of V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst for selective catalytic reduction of NO$_x$ by NH$_3$. *ACS Catal.* 2020, 10, 2747–2753. [CrossRef]

37. Nam, K.B.; Yeo, J.H.; Hong, S.C. Study of the phosphorus deactivation effect and resistance of vanadium-based catalysts. *Ind. Eng. Chem. Res.* 2019, 58, 18930–18941. [CrossRef]

38. Putluru, S.S.R.; Schill, L.; Godiksen, A.; Poredy, R.; Mossin, S.; Jensen, A.D.; Fehrmann, R. Promoted V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO with NH$_3$ at low temperatures. *Appl. Catal. B* 2016, 183, 282–290. [CrossRef]

39. Bosch, F.J.H. Formation and control of nitrogen oxides. *Catal. Today* 1988, 2, 369–379.

40. Amiridis, M.D.; Duevel, R.V.; Wachs, I.E. The effect of metal oxide additives on the activity of V$_2$O$_5$/TiO$_2$ catalysts for the selective catalytic reduction of nitric oxide by ammonia. *Appl. Catal. B* 1999, 20, 111–122. [CrossRef]

41. Roy, S.; Hegde, M.S.; Madras, G.J.A.E. Catalysis for NO$_x$ abatement. *Appl. Energy* 2009, 86, 2283–2297. [CrossRef]

42. Song, I.; Youn, S.; Lee, H.; Lee, S.G.; Cho, S.J.; Kim, D.H. Effects of microporous TiO$_2$ support on the catalytic and structural properties of V$_2$O$_5$/microporous TiO$_2$ for the selective catalytic reduction of NO by NH$_3$. *Appl. Catal. B* 2017, 210, 421–431. [CrossRef]

43. Youn, S.; Song, I.; Lee, H.; Cho, S.J.; Kim, D.H. Effect of pore structure of TiO$_2$ on the SO$_2$ poisoning over V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO$_x$ with NH$_3$. *Catal. Today* 2018, 303, 19–24. [CrossRef]

44. Liu, X.; Li, J.; Li, X.; Peng, Y.; Wang, H.; Jiang, X.; Wang, L. NH$_3$ selective catalytic reduction of NO: A large surface TiO$_2$ support and its promotion of V$_2$O$_5$ dispersion on the prepared catalyst. *Chin. J. Catal.* 2016, 37, 878–887. [CrossRef]

45. Tran, T.; Yu, J.; Gan, L.; Guo, F.; Phan, D.; Xu, G. Upgrading V$_2$O$_5$-WO$_3$/TiO$_2$ deNO$_x$ catalyst with TiO$_2$-SiO$_2$ support prepared from Ti-bearing blast furnace slag. *Catalysts* 2016, 6, 56. [CrossRef]

46. Ferjani, W.; Boudali, L.K.; Delahay, G.; Petitto, C. Reduction of nitrogen oxide by ammonia over vanadium supported on mixed tungsten-titanium-pillared clays. *Chem. Lett.* 2016, 45, 872–874. [CrossRef]

47. Li, X.; Wu, Z.; Zeng, Y.; Han, J.; Zhang, S.; Zhong, Q. Reduced TiO$_2$ inducing highly active V$_2$O$_5$ species for selective catalytic reduction of NO by NH$_3$. *Chem. Phys. Lett.* 2020, 750, 137494. [CrossRef]

48. da Cunha, B.N.; Gonçalves, A.M.; da Silveira, R.G.; Urquieta-Gonzalez, E.A.; Nunes, L.M. The influence of a silica pillar in lamellar tetratitanate for selective catalytic reduction of NO$_x$ using NH$_3$. *Mater. Res. Bull.* 2015, 61, 124–129. [CrossRef]

49. Bukowski, A.; Schill, L.; Nietsens, D.; Mossin, S.; Riisager, A.; Albert, J. NH$_3$-SCR of NO with novel active, supported vanadium-containing Keggin-type heteropolyacid catalysts. *React. Chem. Eng.* 2020, 5, 935–948. [CrossRef]

50. Mejía-Centeno, I.; Castillo, S.; Camposeco, R.; Marin, J.; García, L.A.; Fuentes, G.A. Activity and selectivity of V$_2$O$_5$/H$_2$Ti$_3$O$_7$, V$_2$O$_5$-WO$_3$/H$_2$Ti$_3$O$_7$ and Al$_2$O$_3$/H$_2$Ti$_3$O$_7$ model catalysts during the SCR-NO with NH$_3$. *Chem. Eng. J.* 2015, 264, 873–885. [CrossRef]

51. Cheng, J.; Song, Y.; Ye, Q.; Cheng, S.; Kang, T.; Dai, H. A mechanistic investigation on the selective catalytic reduction of NO with ammonia over the V- Ce/ Ti PILC catalysts. *Mol. Catal.* 2018, 445, 111–123. [CrossRef]

52. Vuong, T.H.; Radnik, J.; Rabeah, J.; Bentrup, U.; Schneider, M.; Atia, H.; Armbruster, U.; Grünert, W.; Brückner, A. Efficient VO$_x$/Ce$_{1-x}$Ti$_3$O$_7$ catalysts for low-temperature NH$_3$-SCR: Reaction mechanism and active sites assessed by in situ/operando spectroscopy. *ACS Catal.* 2017, 7, 1693–1705. [CrossRef]

53. Lian, Z.; Liu, F.; He, H. Effect of preparation methods on the activity of VO$_x$/CeO$_2$ catalysts for the selective catalytic reduction of NO$_x$ with NH$_3$. *Catal. Sci. Technol.* 2015, 5, 389–396. [CrossRef]

54. Lian, Z.; Liu, F.; He, H. Enhanced activity of Ti-modified V$_2$O$_5$/CeO$_2$ catalyst for the selective catalytic reduction of NO$_x$ with NH$_3$. *Ind. Eng. Chem. Res.* 2014, 53, 19506–19511. [CrossRef]

55. Lian, Z.; Liu, F.; He, H.; Liu, K. Nb-doped VO$_x$/CeO$_2$ catalyst for NH$_3$-SCR of NO$_x$ at low temperatures. *RSC Adv.* 2015, 5, 37675–37681. [CrossRef]

56. Lian, Z.; Liu, F.; Shan, W.; He, H. Improvement of Nb doping on SO$_2$ resistance of VO$_x$/CeO$_2$ catalyst for the selective catalytic reduction of NO$_x$ with NH$_3$. *J. Phys. Chem. C* 2017, 121, 7803–7809. [CrossRef]
57. Liu, S.; Wang, H.; Wei, Y.; Zhang, R.; Royer, S. Morphology-Oriented ZrO2-Supported Vanadium Oxide for the NH3-SCR Process: Importance of Structural and Textural Properties. ACS Appl. Mater. Interfaces 2019, 11, 22240–22254. [CrossRef]

58. Thanh Huyen, V.; Radnik, J.; Kondratenko, E.; Schneider, M.; Armbruster, U.; Brueckner, A. Structure-reactivity relationships in VOxyCe1-xZrO2 catalysts used for low-temperature NH3-SCR of NO. Appl. Catal. B 2016, 197, 159–167.

59. Zhao, L.K.; Li, C.T.; Li, S.H.; Wang, Y.; Zhang, J.Y.; Wang, T.; Zeng, G.M. Simultaneous removal of elemental mercury and NO in simulated flue gas over V2O5/ZrO2-CeO2 catalyst. Appl. Catal. B 2016, 198, 420–430. [CrossRef]

60. Zhao, L.; Li, C.; Du, X.; Zeng, G.; Gao, L.; Zhai, Y.; Wang, T.; Zhang, J. Effect of Co addition on the performance and structure of V-ZrCe catalyst for simultaneous removal of NO and Hg0 in simulated flue gas. Appl. Surf. Sci. 2018, 437, 390–399. [CrossRef]

61. Niu, C.; Wang, Y.; Ren, D.; Xiao, L.; Duan, R.; Wang, B.; Wang, X.; Xu, Y.; Li, Z.; Shi, J.W. The deposition of VWOx on the CuCeOx microflower for the selective catalytic reduction of NOx at low temperatures. J. Colloid Interface Sci. 2020, 561, 808–817. [CrossRef] [PubMed]

62. Keller, S.; Agostini, G.; Antoni, H.; Kreyenschulte, C.R.; Atia, H.; Rabaei, J.; Bentrup, U.; Brueckner, A. The effect of iron and vanadium in VOx/Ce1−xFe2O3-delta catalysts in low-temperature selective catalytic reduction of NOx by ammonia. ChemCatChem 2020, 12, 2440–2451. [CrossRef]

63. Bai, S.; Jiang, S.; Li, H.; Guan, Y. Carbon nanotubes loaded with vanadium oxide for reduction NO with NH3 at low temperature. Chin. J. Chem. Eng. 2015, 23, 516–519. [CrossRef]

64. Bai, S.; Wang, X.; Li, H.; Xu, X.; Liu, M. SO2 promotion in NH3-SCR reaction over V2O5/SiC catalyst at low temperature. Fuel 2017, 194, 36–41. [CrossRef]

65. Yang, W.; Liu, F.; Xie, L.; Lian, Z.; He, H. Effect of V2O5 additive on the SO2 resistance of a Fe2O3/AC catalyst for NH3-SCR of NO at low temperatures. Ind. Eng. Chem. Res. 2016, 55, 2677–2685. [CrossRef]

66. Jiang, L.; Liu, Q.; Ran, G.; Kong, M.; Ren, S.; Yang, J.; Li, J. V2O5-modified Mn-Ce/AC catalyst with high SO2 tolerance for low-temperature NH3-SCR of NO. Chem. Eng. J. 2019, 370, 810–821. [CrossRef]

67. He, Y.; Ford, M.E.; Zhu, M.; Liu, Q.; Tumuluri, U.; Wu, Z.; Wachs, I.E. Influence of catalyst synthesis method on selective catalytic reduction (SCR) of NO by NH3 with V2O5-WO3/TiO2 catalysts. Appl. Catal. B 2016, 193, 141–150. [CrossRef]

68. Shen, M.; Xu, L.; Wang, J.; Li, C.; Wang, W.; Wang, J.; Zhai, Y. Effect of synthesis methods on activity of V2O5/CeO2/WO3-TiO2 catalyst for selective catalytic reduction of NOx with NH3. J. Rare Earths 2016, 34, 259–267. [CrossRef]

69. Cha, W.; Ehrman, S.H.; Jurng, J. Surface phenomenon of CeO2-added V2O5/TiO2 catalyst based chemical vapor condensation (CVC) for enhanced selective catalytic reduction at low temperatures. Chem. Eng. J. 2016, 304, 72–78. [CrossRef]

70. Vuong, T.H.; Radnik, J.; Schneider, M.; Atia, H.; Armbruster, U.; Brückner, A. Effect of support synthesis methods on structure and performance of VOx/Ce2O3 catalysts in low-temperature NH3-SCR of NO. Catal. Commun. 2016, 84, 171–176. [CrossRef]

71. Cheng, K.; Liu, J.; Zhao, Z.; Wei, Y.C.; Duan, A.J. Direct synthesis of V-W-Ti nanoparticle catalysts for selective catalytic reduction of NO with NH3. RSC Adv. 2015, 5, 45172–45183. [CrossRef]

72. Chen, T.; Lin, H.; Guan, B.; Gong, X.; Li, K.; Huang, Z. Promoting the low temperature activity of Ti-V-O catalysts by premixed flame synthesis. Chem. Eng. J. 2016, 296, 45–55. [CrossRef]

73. Song, L.; Lee, H.; Kim, D.H. Rotation-assisted hydrothermal synthesis of thermally stable multiwalled titanate nanotubes and their application to selective catalytic reduction of NO with NH3. ACS Appl. Mater. Interfaces 2018, 10, 42249–42257. [CrossRef] [PubMed]

74. Doronkin, D.E.; Benzi, F.; Zheng, L.; Sharapa, D.I.; Amidani, L.; Studt, F.; Roessy, P.W.; Casapu, M.; Deutschmann, O.; Gruenwaldt, J.D. NH3-SCR over V-W/TiO2 investigated by operando X-ray absorption and emission spectroscopy. J. Phys. Chem. C 2019, 123, 14338–14349. [CrossRef]

75. Gan, L.; Chen, J.; Peng, Y.; Yu, J.; Tran, T.; Li, K.; Wang, D.; Xu, G.; Li, J. NOx removal over V2O5/WO3-TiO2 prepared by a grinding method: Influence of the precursor on vanadium dispersion. Ind. Eng. Chem. Res. 2018, 57, 150–157. [CrossRef]

76. Wang, H.; Wang, F.; Chen, X.; Wu, Z. Uniformly active phase loaded selective catalytic reduction catalysts (V2O5/TNTs) with superior alkaline resistance performance. J. Hazard. Mater. 2017, 324, 507–515. [CrossRef]
77. Casanova, M.; Nodari, L.; Sagar, A.; Schermanz, K.; Trovarelli, A. Preparation, characterization and NH3-SCR activity of FeVO4 supported on TiO2-WO3-SiO2. *Appl. Catal. B* **2015**, *176–177*, 699–708. [CrossRef]

78. Liu, X.; Zhao, Z.; Ning, R.; Qin, Y.; Zhu, T.; Liu, F. Ce-doped V2O5-WO3/TiO2 with low vanadium loadings as SCR catalysts and the resistance of H2 and SO2. *Catal. Lett.* **2020**, *150*, 375–383. [CrossRef]

79. Chen, G.; Xu, J.; Yu, H.; Guo, F.; Xie, J.; Wang, Y. Effect of the non-thermal plasma treatment on the structure and SCR activity of vanadium-based catalysts. *Chem. Eng. J.* **2020**, *380*, 122286. [CrossRef]

80. Lian, Z.; Xin, S.; Zhu, N.; Wang, Q.; Xu, J.; Zhang, Y.; Shan, W.; He, H. Effect of treatment atmosphere on the vanadium species of V/TiO2 catalysts for the selective catalytic reduction of NOx with NH3. *Catal. Sci. Technol.* **2020**, *10*, 311–314. [CrossRef]

81. Zhao, X.; Huang, L.; Li, H.R.; Hu, H.; Hu, X.N.; Shi, L.Y.; Zhang, D.S. Promotional effects of zirconium doped CeVO4 for the low-temperature selective catalytic reduction of NOx with NH3. *Appl. Catal. B* **2016**, *183*, 269–281. [CrossRef]

82. Mu, J.; Li, X.; Sun, W.; Fan, S.; Wang, X.; Wang, L.; Qin, M.; Gan, G.; Yin, Z.; Zhang, D. Inductive Effect Boosting Catalytic Performance of Advanced Fe1-xVxO4 Catalysts in Low-Temperature NH3 Selective Catalytic Reduction: Insight into the Structure, Interaction, and Mechanisms. *ACS Catal.* **2018**, *8*, 6760–6774. [CrossRef]

83. Kim, J.; Kim, D.H.; Kwon, D.W.; Ha, H.P. Rational selection of Fe2V4O13 over FeVO4 as a preferred active site on Sb-promoted TiO2 for catalytic NOx reduction with NH3. *Catal. Sci. Technol.* **2018**, *8*, 4774–4787. [CrossRef]

84. Marberger, A.; Ferri, D.; Sagar, A.; Schermanz, K.; Kroecher, O. Generation of NH3-active catalysts from decomposition of supported FeVO4. *ACS Catal.* **2015**, *5*, 4180–4188. [CrossRef]

85. Wu, G.X.; Li, J.; Fang, Z.T.; Lan, L.; Wang, R.; Lin, T.; Gong, M.C.; Chen, Y.Q. Effect of treatment atmosphere on the structure, interaction, and mechanisms. *ACS Catal.* **2015**, *6*, 5604–5615. [CrossRef]

86. Casanova, M.; Llorca, J.; Sagar, A.; Schermanz, K.; Trovarelli, A. Mixed iron-erbium vanadate NH3-SCR catalysts. *Catal. Today* **2015**, *241*, 159–168. [CrossRef]

87. Gillot, S.; Tricot, G.; Vezin, H.; Dacquin, J.P.; Dujardin, C.; Granger, P. Development of stable and efficient CeVO4 systems for the selective reduction of NOx by ammonia: Structure-activity relationship. *Appl. Catal. B* **2017**, *218*, 338–348. [CrossRef]

88. Zhao, X.; Huang, L.; Namuangruk, S.; Hu, H.; Hu, X.N.; Shi, L.Y.; Zhang, D.S. Morphology-dependent performance of Zr-CeVO4/TiO2 for selective catalytic reduction of NO with NH3. *Catal. Sci. Technol.* **2016**, *6*, 5543–5553. [CrossRef]

89. Gao, S.; Wang, P.; Yu, F.; Wang, H.; Wu, Z. Dual resistance to alkali metals and SO2: Vanadium and cerium supported on sulfated zirconia as an efficient catalyst for NH3-SCR. *Catal. Sci. Technol.* **2016**, *6*, 8148–8156. [CrossRef]

90. Huang, X.; Zhang, G.; Dong, F.; Tang, Z. The remarkable promotional effect of Sn on CeVO4 catalysts for wide temperature NH3-SCR process by citric acid-assisted solvothermal synthesis and post-hydrothermal treatment. *Catal. Sci. Technol.* **2018**, *8*, 5604–5615. [CrossRef]

91. Kim, J.; Kwon, D.W.; Lee, S.; Ha, H.P. Exploration of surface properties of Sb-promoted copper vanadate catalysts for selective catalytic reduction of NOx by NH3. *Appl. Catal. B* **2018**, *236*, 314–325. [CrossRef]

92. Kim, J.; Lee, S.; Kwon, D.W.; Lee, K.Y.; Ha, H.P. SO32-/SO42− functionalization-tailorable catalytic surface features of Sb-promoted Cu3V2O8 on TiO2 for selective catalytic reduction of NOx with NH3. *Appl. Catal. A* **2019**, *570*, 355–366. [CrossRef]

93. Gillot, S.; Tricot, G.; Vezin, H.; Dacquin, J.P.; Dujardin, C.; Granger, P. Induced effect of tungsten incorporation on the catalytic properties of CeVO4 systems for the selective reduction of NOx by ammonia. *Appl. Catal. B* **2018**, *234*, 318–328. [CrossRef]

94. Marberger, A.; Ferri, D.; Elsener, M.; Sagar, A.; Artner, C.; Schermanz, K.; Kroecher, O. Relationship between structures and activities of supported metal vanadates for the selective catalytic reduction of NO by NH3. *Appl. Catal. B* **2017**, *218*, 731–742. [CrossRef]

95. Wu, G.; Li, J.; Fang, Z.; Lan, L.; Wang, R.; Gong, M.; Chen, Y. FeVO4 nanorods supported TiO2 as a superior catalyst for NH3-SCR reaction in a broad temperature range. *Catal. Commun.* **2015**, *64*, 75–79. [CrossRef]
96. Huang, X.; Zhang, G.; Tang, Z. Facile fabrication of Ce/V-modified multi-channel TiO₂ nanotubes and their enhanced selective catalytic reduction performance. *Chem. Asian J.* 2020, 15, 371–379. [CrossRef]

97. Lee, S.G.; Lee, H.J.; Song, I.; Youn, S.; Kim, D.H.; Cho, S.J. Suppressed N₂O formation during NH₃ selective catalytic reduction using vanadium on zeolitic microporous TiO₂. *Sci. Rep.* 2015, 5, 12702. [CrossRef]

98. Zhang, T.; Chang, H.; Li, K.; Peng, Y.; Li, X.; Li, J. Different exposed facets VOₓ/CeO₂ catalysts for the selective catalytic reduction of NO with NH₃. *Chem. Eng. J.* 2018, 349, 184–191. [CrossRef]

99. Song, L.; Zhang, R.; Zang, S.; He, H.; Su, Y.; Qiu, W.; Sun, X. Activity of selective catalytic reduction of NO over V₂O₅/TiO₂ catalysts preferentially exposed anatase [001] and [101] facets. *Catal. Lett.* 2017, 147, 934–945. [CrossRef]

100. Boningari, T.; Pappas, D.K.; Smirniotis, P. Metal oxide-confined interwoven titania nanotubes Mn/TiO₂ for the selective catalytic reduction of NO with NH₃ at low temperature. *Catal. Sci. Technol.* 2015, 5, 4280–4288. [CrossRef]

101. Shan, W.; Song, H. Catalysts for the selective catalytic reduction of NO₃⁻ with NH₃ at low temperature. *Catal. Sci. Technol.* 2015, 5, 4280–4288. [CrossRef]

102. Forzatti, P. Present status and perspectives in de-NO₃ SCR catalysis. *Appl. Catal. A* 2001, 222, 221–236. [CrossRef]

103. Shan, W.; Yu, Y.; Zhang, Y.; He, G.; Peng, Y.; Li, J.; He, H. Theory and practice of metal oxide catalyst design for the selective catalytic reduction of NO with NH₃. *Catal. Today* 2020, in press.

104. Zhu, M.; Lai, J.K.; Tumuluri, U.; Wu, Z.; Wachs, I.E. Nature of active sites and surface intermediates during SCR of NO with NH₃ by supported V₂O₅-WO₃/TiO₂ catalysts. *J. Am. Chem. Soc.* 2017, 139, 15624–15627. [CrossRef]

105. Marberger, A.; Ferri, D.; Elsener, M.; Krocher, O. The significance of Lewis acid sites for the selective catalytic reduction of nitric oxide on vanadium-based catalysts. *Angew. Chem. Int. Ed.* 2016, 55, 11989–11994. [CrossRef]

106. Song, I.; Lee, H.; Jeon, S.W.; Kim, D.H. Understanding the dynamic behavior of acid sites on TiO₂-supported vanadia catalysts via operando DRIFTS under SCR-relevant conditions. *J. Catal.* 2020, 382, 269–279. [CrossRef]

107. Liu, H.; You, C.; Wang, H. Time-resolved in-situ IR and DFT study: NH₃ adsorption and redox cycle of acid site on vanadium-based catalysts for NO abatement via selective catalytic reduction. *Chem. Eng. J.* 2020, 382, 122756. [CrossRef]

108. Kong, M.; Liu, Q.; Jiang, L.; Tong, W.; Yang, J.; Ren, S.; Li, J.; Tian, Y. K⁺ deactivation of V₂O₅-WO₃/TiO₂ catalyst during selective catalytic reduction of NO with NH₃: Effect of vanadium content. *Chem. Eng. J.* 2019, 370, 518–526. [CrossRef]

109. He, G.; Lian, Z.; Yu, Y.; Yang, Y.; Liu, K.; Shi, X.; Yan, Z.; Shan, W.; He, H. Polymeric vanadyl species determine the low-temperature activity of V-based catalysts for the SCR of NOₓ with NH₃. *Sci. Adv.* 2018, 4, eaau4637. [CrossRef]

110. Jaegers, N.R.; Lai, J.K.; He, Y.; Walter, E.; Dixon, D.A.; Vasiliiu, M.; Chen, Y.; Wang, C.; Hu, M.Y.; Mueller, K.T.; et al. Mechanism by which tungsten oxide promotes the activity of supported V₂O₅/TiO₂ catalysts for NOₓ abatement: Structural effects revealed by V-51 MAS NMR spectroscopy. *Angew. Chem. Int. Ed.* 2019, 58, 12609–12616. [CrossRef]

111. Liu, K.; Yan, Z.; He, H.; Feng, Q.; Shan, W. The effects of H₂O on a vanadium-based catalyst for NH₃-SCR at low temperatures: A quantitative study of the reaction pathway and active sites. *Catal. Sci. Technol.* 2019, 9, 5593–5604. [CrossRef]

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.