Review

Research Status and Prospect on Vanadium-Based Catalysts for NH$_3$-SCR Denitration

Jie Zhang, Xiangcheng Li *, Pingan Chen * and Boquan Zhu *

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China; zzzjwust@163.com
* Correspondence: lixiangcheng@wust.edu.cn (X.L.); cpa_0502@163.com (P.C.); zbqref@263.net (B.Z.)
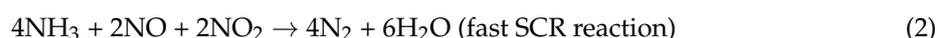
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Abstract: Selective catalytic reduction of NO$_x$ with NH$_3$ is one of the most widely used technologies in denitration. Vanadium-based catalysts have been extensively studied for the deNO$_x$ process. V$_2$O$_5$/WO$_3$(MoO$_3$)TiO$_2$ as a commercial catalyst has excellent catalytic activity in the medium temperature range. However, it has usually faced several problems in practical industrial applications, including narrow windows of operation temperatures, and the deactivation of catalysts. The modification of vanadium-based catalysts will be the focus in future research. In this paper, the chemical composition of vanadium-based catalysts, catalytic mechanism, the broadening of the temperature range, and the improvement of erosion resistance are reviewed. Furthermore, the effects of four major systems of copper, iron, cerium and manganese on the modification of vanadium-based catalysts are introduced and analyzed. It is worth noting that the addition of modified elements as promoters has greatly improved the catalytic performance. They can enhance the surface acidity, which leads to the increasing adsorption capacity of NH$_3$. Surface defects and oxygen vacancies have also been increased, resulting in more active sites. Finally, the future development of vanadium-based catalysts for denitration is prospected. It is indicated that the main purpose for the research of vanadium-based modification will help to obtain safe, environmentally friendly, efficient, and economical catalysts.

Keywords: vanadium-based catalysts; NH$_3$-SCR; NO$_x$; modification

1. Introduction

Nitrogen oxides (NO$_x$) are one of major air pollutants that could cause great harm to the ecological environment and human health. How to remove NO$_x$ effectively is a significant issue of environmental protection. Currently, there are three kinds of reductant for the selective catalytic reduction of NO$_x$: NH$_3$, Urea and HC. NH$_3$-SCR (selective catalytic reduction with ammonia) is the most mature industrial technology at present, and its main reaction process [1–3] is:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \text{ (standard SCR reaction)} \tag{1}$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \text{ (fast SCR reaction)} \tag{2}$$

The technology has been used in hundreds of large power plants in the United States, Germany, and Japan. Environmental conditions have a great impact on this technology. For example, it is important to control oxygen content of the exhaust appropriately for NH$_3$-SCR. In the absence of O$_2$, the reducing agent cannot reduce NO. When the oxygen content of the exhaust is below 5%, the catalytic reduction reaction of NH$_3$ can be carried out to convert NO$_x$ into N$_2$ and H$_2$O. When the oxygen concentration is too high, the activity of the catalyst will be reduced, and NH$_3$ will be oxidized to NO$_2$, resulting in new pollution.

The catalyst is the key to determining the reactivity of NH_3-SCR under the proper external conditions. In the 1960s, a study on exhaust gas-purifying catalysts was started. A three-way catalyst (TWC) consisting of precious metals was researched in the initial stage. Although the catalytic effect is ideal, considering the cost and the source of precious metals, the direction has shifted to transition metal oxide catalysts. Vanadium-based catalysts are used due to the high activity of SCR reactions. With the continuous improvement of environmental protection and energy awareness and the increasing demand for low NO_x emissions, the traditional vanadium-based catalysts are no longer satisfactory. The performance improvement of vanadium-based catalysts has become the focus of research.

In this paper, the characteristics and performance improvement of vanadium-based catalysts is the main line. The research progress of vanadium-based catalysts at home and abroad is reviewed. The advantages and disadvantages, mechanism, and improvement methods are summarized. The development of vanadium-based catalysts for denitrification is prospected.

2. Composition of Vanadium Based Catalyst

The catalyst is obtained in such a way that the active component and promoter are loaded on catalyst support. The catalyst support is believed to be important for SCR reaction because of its high surface areas, good thermal stability, and high active substance dispersion on surfaces [4]. In general, TiO_2–anatase is widely used as a support for vanadium-based catalyst because of its great SO_2 resistance and excellent dispersion of V_2O_5. A small amount of sulfate species loaded on the support enhances the surface acidity of the V_2O_5/TiO_2 catalyst, increases the amount of adsorbed NH_3, and improves the SCR activity [5,6]. However, pure TiO_2 is poorly active during the SCR reaction due to its weak acidity and poor redox ability. Additionally, TiO_2 will transform from anatase to rutile at high temperatures, which will affect the stability of the support. Therefore, some modifications have been investigated to overcome these defects. Adrian, M. et al. [7] chose TiO_2-WO_3-SiO_2 as a catalyst support for optimization, using rare metal to inhibit the phase transition of titanium dioxide, to avoid high temperature sintering and surface area loss, and improve the structural strength of the support. At the same time, SiO_2 is beneficial to SO_2 resistance. Cheng, J. et al. [8] synthesized TiO_2-PILC as a catalyst support for the SCR of NO_x with NH_3 due to pillared interlayered clays' large specific surface areas, acidity, and high thermal stability. Other catalyst support is also helpful for the performance of the catalyst, such as TiO_2-pal [4], and activated carbon (AC) [9].

The active component is the dominant factor affecting vanadium-based catalyst performance, and it can be divided into single vanadium oxide VO_x [10,11] and multi-metal oxide compounds such as VO_x-WO_3 [12], VO_x-CeO_x [8]. V_2O_5 catalyst is a kind of structure-sensitive catalyst, whose activity is affected by the structure and coverage of V_2O_5, the crystal form of catalyst support, and the modification element. Increasing the amount of V_2O_5 added can help to improve the catalytic activity. However, V_2O_5 will promote the transformation of anatase to rutile, which is not conducive to the thermal stability of the catalyst, resulting in the shortened life of the catalyst and the decrease of selectivity [13]. In view of this, the content of vanadium in the commercial catalyst VO_x-WO_x/TiO_2 is generally limited to less than 2.6%. The coverage rate is also an important parameter, which can be adjusted by the V loading or the calcination temperature [14]. The coverage rate for ideal V_2O_5-WO_3/TiO_2 catalysts is 25–50%. Below 25% indicates that the vanadium content is too low or the surface area is too high and the catalyst activity is low. With coverage of more than 50%, the stability of the catalyst and the conversion of NO_x at high temperatures cannot be guaranteed [7,14]. The vanadium coverage of conventional catalysts is below the dispersion limit that monolayer 6–7 atom/nm^2 to avoid the crystalline V_2O_5 [15]. It is generally believed that in the dry anatase surface at low loading V_2O_5, the dehydrated surface vanadium generally tend to possess isolated four-fold coordination. The isolated VO_4 units consist of one terminal V=O bond and three bridging V-O-Ti bonds, as shown in Figure 1a. As the coverage increases, the number of V-O-V bridges per V increases. In practical application, the vanadium species mainly exists in the form of polyvanadate, as shown in Figure 1b. This species has higher SCR reactivity than the

monomer $(Ti-O)_3V=O$ [3,15,16]. At high loading V_2O_5, crystalline vanadia is generated on sulfated TiO_2 (Figure 1c). In view of the volatilization of vanadium at high temperatures, the use of metal vanadate $(MeVO_4)$ in the active phase can increase the melting point of the catalyst [17,18]. Moreover, Zhou, X. et al. [19] synthesize the V@Mn-Fe/ATP catalyst with a similar core-shell structure successfully. It was found that the V_2O_5 layer as a coating might protect other active metals of the catalyst.
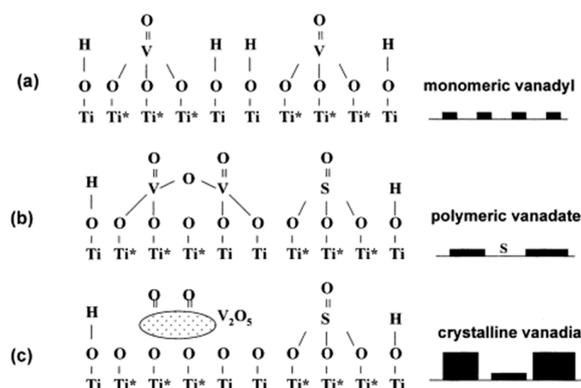

Figure 1. A schematic of the transformation of V_2O_5 on titania: (**a**) low loading V_2O_5 supported on sulfur-free TiO_2; (**b**) low loading V_2O_5 supported on sulfated TiO_2 and (**c**) high loading V_2O_5 supported on sulfated TiO_2 (Ti*, basic site; Ti, neutral site). Reproduced with permission [20]. Copyright 2000, Elsevier.

3. NH₃-SCR Reaction Mechanism of Vanadium-Based Catalyst

Zhu, M. et al. [2] used elemental tagging to study the SCR reaction pathway of vanadium-based catalysis and found that the SCR reaction occurs at the surface $V^{5+}O_4$ site. This is shown in Figure 2, which exhibits a schematic diagram of the standard SCR reaction and indicates that SCR reaction is divided into three steps. First, NH_3 adsorption is observed on the surface of the acid center. Next, the adsorbed ammonia reacts with NO to form an intermedium. The intermedium can decompose to N_2 and H_2O and reduce surface $V^{5+}O_4$ sites. Finally, the reduced $V^{4+}O_3$ is reoxidized by O_2. Through the kinetic study, the rate-determining step of the SCR reaction is that the V^{5+} on the surface is reduced to V^{4+} by NO and NH_3, particularly the breaking of N–H bonds during the process of formation or decomposition of the intermedium. The vanadium-based catalyst V_2O_5-WO_3/TiO_2 has been commercialized and applied in some thermal power plants. In V_2O_5-WO_3/TiO_2 catalysts, the $O=VO_3$ site is involved in the redox cycle, which is the most important for the SCR reaction. The $O=WO_4$ site enhances the surface acidity of the catalyst and promotes the adsorption of NH_3 [12]. Tungsten oxide as a promoter has two primary roles in catalysis: it restrains the generation of bulk polymeric V aggregates and retains Brønsted acid sites at high temperatures [21].
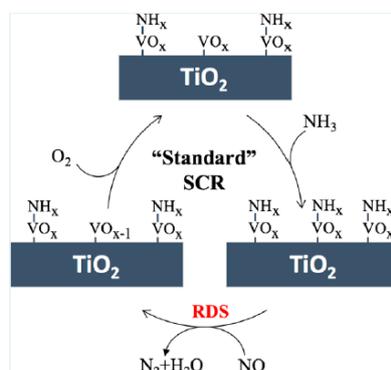

Figure 2. Schematic diagram of the standard SCR reaction. Reproduced with permission [2]. Copyright 2017, American Chemical Society.

Although vanadium-based catalysts have been used in industrial applications, the reaction mechanism for vanadium-based catalysts remains controversial. It is mainly divided into two theories: the Langmuri-Hinshelwood theory (L-H theory) and the Eley-Rideal theory (E-R theory). It is widely believed that the vanadium-based catalyst selectively reduces NO_x via the E-R mechanism at medium-high temperature. A schematic diagram of the NH_3-SCR reaction mechanism is shown in Figure 3. Although ammonia is adsorbed on both Lewis acid sites and Brønsted acid sites, NH_3 is more prone to be adsorbed at the Brønsted acid sites than at the Lewis acid sites. NH_3 forms NH^{4+} on the Brønsted acid site (V–OH) and reacts with the V=O group to generate intermediate products, and then decomposes into N_2 and H_2O. However, NH_3 adsorption on Lewis acid sites will produce N_2O [3].
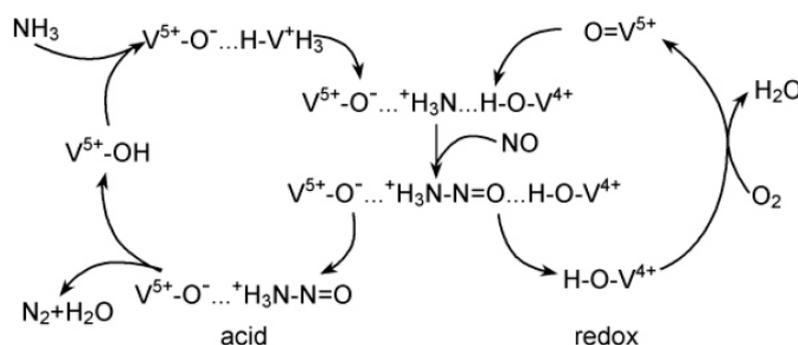

Figure 3. Schematic diagram of NH_3-SCR reaction mechanism. Reproduced with permission [22]. Copyright 1995, Elsevier.

Aside from the Langmuri-Hinshelwood model and the Eley-Rideal model, a surface Mar-van Krevelen reaction mechanism has been proposed for the SCR reaction. According to the Mar-Van Krevelen mechanism, SCR reaction divides into three steps: adsorption, migration, and reoxidation. There are two different types of centers that prevail on the SCR catalysts: S1 sites, related to vanadium and its redox cycle, and S2 sites, used to store ammonia and nitrates [23]. However, there is controversy around the step of vanadium reoxidation. According to the sites of detached gaseous oxygen, two different possibilities for vanadium reoxidation steps were proposed: in one case that the vacancy in the vanadia lattice is filled using molecular oxygen, and the other through the creation of a vacancy in the titania lattice [24].

In fact, the SCR reaction mechanism is closely related to the reaction temperature. With different reaction temperatures, the number and distribution of the active sites of the catalysts are different, and the types, quantities and distributions of the acids are not the same. Therefore, the reaction mechanism of vanadium-based catalysts may also change with different reaction temperatures. It is worth noting that current studies only focus on the formation of acid centers and the activity of acids in acid-base mechanism. It also has a certain significance to study the effect of alkaline position on the adsorption and the activity [3].

4. Performance Improvement of Vanadium Based Catalysts

Commercial vanadium-based catalysts are widely used in industry due to their high activity and excellent SO_2 resistance. However, they have a narrow activity window, and weak ability for resisting VO_X species to thermal sintering. The metal oxide is also over-oxidized, which not only oxidizes NH_3 to N_2O and NO, but also oxidizes SO_2 to SO_3. The generated SO_3 continues to react with NH_3 to generate ammonium sulfate species, thereby plugging the pores and masking the active sites, thus decreasing the activity of the SCR reaction [25]. The inevitable soot and some alkali metals in factory waste can also affect the activity of catalysts and even lead to deactivation of catalysts [4,5,26]. The evaluation of vanadium-based catalytic activity is shown in Figure 4. It can be seen that the NO_x conversion rate of conventional catalysts is higher than 90% at 300–400 °C, and has little effect

in the presence of SO_2. However, through experiments, we found that the longer the SO_2 exists, the greater the decrease of catalyst activity as shown in Figure 4b. In this case, the performance improvement of vanadium-based catalysts has been the focus of research. In order to improve the activity of vanadium-based catalysts, the method usually has been adopted by changing the catalyst preparation, improving the performance of the support, adding modification elements and so on.
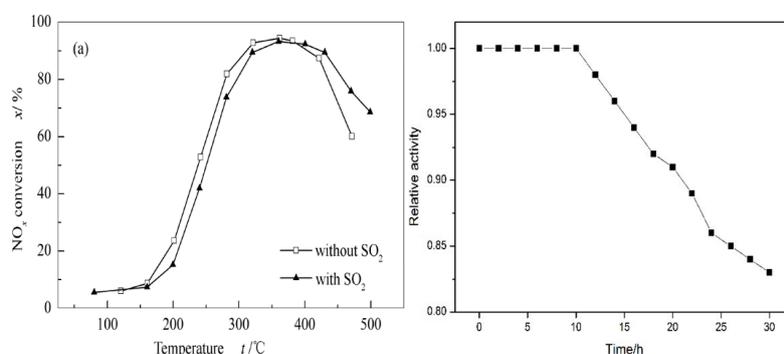

Figure 4. (**a**) NO_x conversion rate under different conditions [17]; (**b**) The relative activity of SO_2 varies with time.

Usually the preparation of catalysts requires drying and calcining, and other processes. Some catalysts are activated by calcination. The calcination temperature affects the crystal structure of the catalyst. The adsorption sites and the adsorption numbers of different crystal planes are different. The surface sites' variation lie with the nature of the oxide, preparative method used, conditions of activation, and impurities [27]. At the same time, both lattice defects and inhomogeneous surfaces have an effect on the catalytic properties.

The crystal form of catalyst support has a significant influence on SCR reactions, for example, TiO_2-anatase has higher dispersibility to active components than TiO_2-rutile and leads to greater performance. The methods of preparing catalyst supports include impregnation, coprecipitation, hydrothermal, and sol-gel. The impregnation method is the most widely used method because of its simple and easily-operated process. These methods mainly control the particle size and morphology of the support, as well as the binding strength of active components to the support, thus affecting the dispersion of active components and the activity of the catalyst. Pappas, D.K. et al. [28] have used the alkaline hydrothermal method to prepare titanium nanotubes and co-precipitation to prepare spherical nanoparticles and nanotubes for comparison. It was found that different forms of supports have certain effects on the SCR reaction. Using titanium nanotubes as support has a better effect than spherical titanium nanoparticles. This is because the multilayer structure of the titanium nanotube can provide greater surface area to facilitate the dispersion of active components, so as to provide more active sites. Vuong, T.H. et al. prepared CeO_2 supports by a citrate or a precipitation method and then got loading V/CeO_2 catalysts by wet impregnation. Comparing with the citrate sol-gel protocol, the mesoporous CeO_2 support prepared by the precipitation method is much more active due to markedly higher surface area, higher concentration of Ce^{3+} bulk species and oxygen vacancies, which are beneficial for oxygen transport through the lattice [10].

Adding a modified element to modify the catalyst is beneficial to improve the performance of vanadium-based catalysts. Different modified elements may cause different effects on the VO_x active sites because of different physical and chemical properties of the surface. The presence of surface acid sites depends on both the specific oxide-supported ligand and the surface density of the metal oxide overlayer [29]. At ambient conditions, vanadium species on titania has distorted the octahedral oxygen environment with one short (V=O) and one long V–O axial bond at low loading V_2O_5 [30]. The theoretical value for monolayer coverage of dehydrated VO_x/TiO_2 catalysts is 7.9 atom/nm^2 [29]. Due to stronger interactions between vanadium and ceria, vanadium oxide species disperse on ceria up to 9 V atom/nm^2 of support determined by Raman Spectroscopy [31]. Vanadia reacts with cerium

oxide to form $CeVO_4$ phase, so two types of vanadium species (VO_x and $CeVO_4$) are dispersed on the surface of cerium dioxide. $CeVO_4$ promotes the formation of Brønsted acid sites while VO_x and CeO_2 provide Lewis acid sites on the surface [32]. However, the formation of Brønsted acid sites is related to vanadium species VO_x in bulk $CeVO_4$ after aging at 500 °C [18]. Therefore, the Lewis acid sites may be converted to the Brønsted acid sites at high temperature SCR reaction. In bulk $CeVO_4$ catalysts, the isolated vanadium species in the tetrahedral coordination are basically stable after the zircon-type structure $CeVO_4$ aging at 500 °C [18]. In the Ce-doped V_2O_5-WO_3/TiO_2 catalyst, the presence of Ce^{3+} creates a charge imbalance, vacancies, and unsaturated chemical bonds, thus increasing the chemisorbed oxygen on the surface. In addition, the coexistence of Ce^{4+} was found to play an important role in the synergic effect on the SCR reaction [33]. At ambient conditions for fresh Fe-V/TiO_2 catalysts, the structures of the vanadium species exist in octahedral (70%) and tetrahedral (30%) coordination [34]. The acid sites on V_2O_5-Fe_2O_3/TiO_2 are mainly derived from Fe_2O_3-TiO_2, so the adsorbed NH_3 prefer to be activated by Fe^{3+}, and then V^{5+} accelerate the regeneration of Fe^{3+} [35]. In $FeVO_4$/TiO_2 catalysts, the $FeVO_4$ loading amount should be less than 9 wt% to avoid exceeding the monolayer dispersion limit. The Fe^{3+}-O-V^{5+} linkages with a low coordination number of vanadium atoms are associated with structural defects on the surface. The presence of an electronic inductive effect between Fe^{3+} and V^{5+} was beneficial for high $deNO_x$ efficiency and N_2 selectivity [36]. At low temperatures, $FeVO_4$ shows low activity for SCR in $FeVO_4$/TiO_2-WO_3-SiO_2 catalysts. However, in the decomposition of $FeVO_4$, the VO_x species exhibits higher SCR activity. So, the active species for SCR is not $FeVO_4$ but VO_x species [37]. The presence of iron can be useful in altering the electron density of the VO_x surface species and inducing more Lewis acid sites and Brønsted acid sites for SCR reaction [38]. Currently, in the catalytic denitrification reaction of manganese-based bimetallic oxide catalysts, Mn-OH as a Brønsted acid site adsorbs NH_3 to form NH_4^+. NH_4^+ is then reacted with NO to create N_2, H_2O and Mn^{3+}–OH. Finally, Mn^{3+} is reoxidized to regenerate Mn^{4+} [39]. The addition of Mn shows a promoting effect on the activity of the V_2O_5/TiO_2 catalyst because manganese oxides contain various valence states, facilitating the completing of the catalytic cycle. As promoter, the ideal loading of Mn is about 2% for V_2O_5/TiO_2 catalysts to avoid the oxidation of NH_3 at high temperatures. The presence of the synergetic effect between V and Mn contributes the improvement of SCR activity. The redox cycle (V^{4+} + Mn^{4+} ↔ V^{5+} + Mn^{3+}) reduces the energy required for electron transfer between Mn and V active sites, and promotes the adsorption and activation of NH_3 and NO. Mn^{3+} is conducive to NH_3-SCR reactions due to its ability to induce the formation of more surface chemisorbed oxygen [40]. In Cu-V/TiO_2 catalysts, the copper species exist mainly as Cu^{2+} in CuV_2O_6, $Cu_2V_2O_7$ or CuO. Different bimetallic copper vanadate oxides have different configurations, for example, distorted octahedral VO_6 sub-units and tetrahedral VO_4 sub-units. VO_4 units are more convenient to access to NH_3 due to their open V environment. By introducing copper species, strong acid sites are increased. It is worth noting that Lewis acid sites are the strong acid sites in Cu–V/TiO_2 catalyst [21,41].

The performance improvement of vanadium-based catalysts is mainly in the following two directions. The first is to widen the temperature window of vanadium-based catalysis, so that it can guarantee the activity of the medium-temperature section and have very good low-temperature activity at the same time. The second is to improve the resistance to sulfate poisoning of vanadium-based catalysts and the erosion ability of water and alkaline metals. Many researchers adopted different methods of improvement and achieved varying results.

4.1. The Broadening of the Temperature Ranges

In practice, the temperature of exhaust gas is about 200 °C. Therefore, the broadening of the temperature range is mainly important for the low temperature section. Adding modified elements (Cu, Ce, Fe, Mn, etc.) is a more effective method to solve it.

The Cu based catalyst has good low temperature activity. It has been found that the combination of copper oxide and other metal oxides can obtain better activity. The NO_x conversion rate of the

catalyst for the Cu–V system is described in Figure 5. It can be seen from diagram that at the optimum Cu–V ratio, the conversion of NO_x reaches 90% at 180 °C and nearly 100% at 220 °C [6]. The synergistic effect of Cu and V alleviated the influence of VO_x aggregation on TiO_2 crystal form, enhanced the adsorption capacity of the catalyst surface, and facilitated to the SCR reaction at low temperatures. However, Cu is conducive to forming $CuSO_4$ with SO_2, and the ability of resisting SO_2 poisoning is poor [5,26].
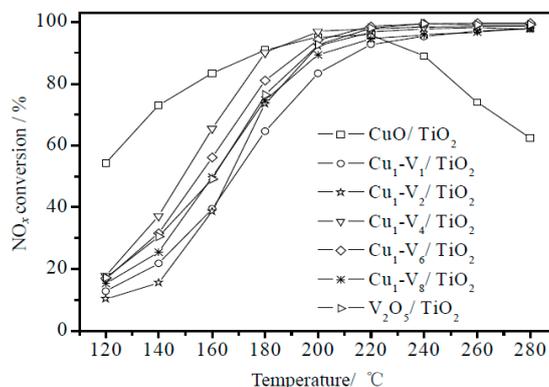

Figure 5. Conversion rate of NO_x at different reaction temperatures [6].

Ce, as a rare earth element, has been studied more in recent years. It has some kind of role of "backup chemical bond" due to the variability of the coordination number. As a modified element, it could facilitate the valence of vanadium species rapidly changing by a redox cycle of $V^{5+} + Ce^{3+} \leftrightarrow V^{4+} + Ce^{4+}$. There are experiments using $CeVO_4$ as a precursor loaded onto the support and compared with the performance of V_2O_5/TiO_2 [7,18]. It shows that the catalyst has a high catalytic activity and a wide temperature window with the best Ce content and a suitable calcination temperature (vanadate decomposition temperature). The activity evaluation of the catalyst with different calcining temperatures in fast conditions is shown in Figure 6. It exhibits that the NO_x conversion rate reaches over 90% at the optimum heat treatment temperature, from 200–450 °C. The calcined $CeVO_4$ exhibited better NO conversion and N_2 selectivity. The redox ability of Ce can increase the surface acidity of the catalyst and improve the storage capacity of oxygen. Ce^{4+}/Ce^{3+} can form solid solutions with other oxides to increase the active sites. Meanwhile, Ce can effectively reduce the sintering tendency [7,42]. In addition, the activity distribution of V_2O_5/CeO_2 mixed oxides is somewhat complex. The existence of $CeVO_4$ and the correlation of the V–O–Ce subsequently constitute two systems: VO_x/CeO_2 and $CeVO_4/CeO_2$. The coexistence of low concentration of Ce^{4+} species assists to enhance the rate NO conversion to nitrogen [18]. And the synergistic effect of two oxides of CeO_2 and V_2O_5 generated by the decomposition of cerium vanadate promotes redox cycle and improves the activity of the catalyst.
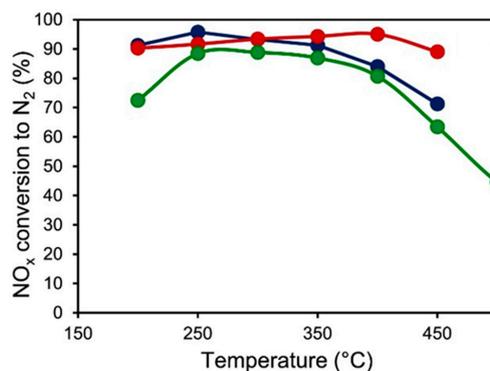

Figure 6. The activity evaluation of the catalyst at different calcining temperatures: after aging at 500 °C (full symbol in red); after aging at 600 °C (full symbol in green); fresh (full symbol in blue). Reproduced with permission [18]. Copyright 2017, Elsevier.

Iron-based catalysts have attracted much attention because of their cheap, nontoxic, and high hydrothermal stability and N_2 selectivity. But at low temperature, they exhibits a poor conversion rate of NO_x. In SCR reactions temperatures below 300 °C, the active site of iron is mainly in the form of isolated Fe^{3+}. When the temperature rises, oligomeric iron oxide clusters, and iron oxide particles become dominant. This contributes more to the SCR reaction and makes it more active. The introduction of Fe can increase the weak acid sites of the catalyst and the NH^{4+} formed by NH_3 in the weak acid sites is more easily attached and activated in the SCR reaction [17]. Nickel added as a modified element could change the electronic environment of the metal surface through the formation of heteroatom bonds, thereby modifying its electronic structure with the ligand effect, improving the surface properties [43]. Wu, G. et al. [44] have conducted experiments by adding nickel to the FeV/Ti catalyst to investigate the effect on the SCR reaction. Figure 7 shows the evaluation of the catalytic activity of different catalysts in the Fe–Ni–V system. It can be seen that, with the optimum proportion, the catalytic activity of NO_x reaches over 90% at 250–550 °C, and the NO_x conversion rate at 280–500 °C reaches 100%. The results show that Ni promotes the interaction between $FeVO_4$ nanoparticles and TiO_2, and improves the acidity and reducing activity. When the content of Ni is 0–0.4, Ni is highly dispersed on the surface of $FeVO_4$. When the content is 0.6–1, Ni reacts with $FeVO_4$ to form nickel-iron spinel, so that more defects and oxygen vacancies are formed on the surface of the catalyst. The addition of Ni affects the grain size, changes the surface properties of the catalyst, has better activity at the test temperature, and can widen the temperature window.
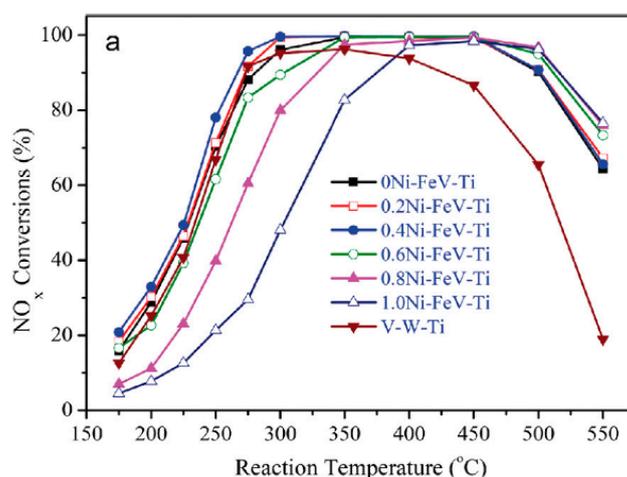

Figure 7. Catalytic activity evaluation of different catalysts in Fe–Ni–V system. Reproduced with permission [44]. Copyright 2017, Elsevier.

Manganese bases have attracted attention due to their high activity at low temperatures. The crystalline phase structure of the manganese-based catalysts prepared by different methods can affect the reactivity of SCR, and the irregular surface structure causes more defects and active sites, thus increasing the reactivity of SCR. Liu, J. et al. [45] have studied the SCR reaction mechanism of manganese-based catalysts and believe that the highly active manganese reacts mainly according to the L–H reaction mechanism at low temperature. Pure MnO_x is unsuitable as a catalyst because of its low surface area and poor thermal stability [46]. However, manganese-based catalysts have lower N_2 selectivity, and are easily deactivated under SO_2 and H_2O conditions, causing irreversible loss of oxidation ability, resulting in the blockage of pores and active sites by ammonium sulfate salts, limiting the further popularization. Therefore, Zheng, Z. et al. [47] utilize the excellent low-temperature performance of MnO_x to make up for the shortcoming of the narrow temperature window of V_2O_5/TiO_2 and prepare an Mn–V–Ce/TiO_2 catalyst. This catalyst uses Mn to provide low-temperature active sites, and Ce and V provide sufficient oxygen vacancies while enhancing the surface acidity, thereby significantly improving the low-temperature activity. As shown in Figure 8, the activity of

Mn–V–Ce/TiO$_2$ catalyst at different temperatures is evaluated. It is found that the NO$_x$ conversion rate is as high as 99.2% at 150 °C, indicating excellent low-temperature activity of the catalyst.
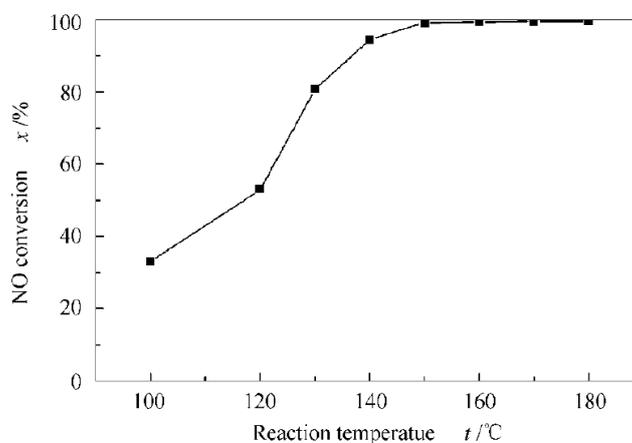

Figure 8. Activity evaluation of Mn-V-Ce/TiO$_2$ catalysts at different temperatures [47].

4.2. The Improvement of Erosion Resistance

V$_2$O$_5$-WO$_3$(MoO$_3$)/TiO$_2$, which has been put into industrial use, is subjected to a lot of erosion in the actual industry environment, one of which is high concentrations of SO$_2$. V$_2$O$_5$ possesses SO$_2$ durability, but SO$_3$ is generated due to peroxidation, and the resulting sulfuric acid (hydrogen) salt will affect the catalyst activity. The addition of WO$_3$ is helpful to increase the Brønsted acid sites, enhance the reaction activity by improving the redox capacity at low temperatures, and to restrain the phase transition, but it still faces erosion of hydrogen sulfate. Li, C. et al. [48] studied the formation and decomposition of ammonium bisulfate over V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts at different temperatures. With the combination of ammonium hydrogen sulfate (ABS) and metal oxides (WO$_3$ and TiO$_2$), electrons deviate from the sulfate, thereby weakening the stability of the ABS and reducing the decomposition temperature. However, the vanadium-generated intermediate VOSO$_4$ makes the sulphate electrons saturated. The presence of NO and O$_2$ could break the bonds inside the ABS, and react with the ammonia species produced in it, allowing the NH$_3$ to be separated from the ABS, accelerating the decomposition of the ABS and competing to inhibit its formation. It was found that the trace ABS on TiO$_2$ had little effect on the NH$_3$-SCR reaction at 300 °C. Under 300 °C, sulfuric acid (hydrogen) ammonia species cover the active sites, masking VOSO$_4$ intermediate products, resulting in a poor NH$_3$-SCR reaction performance. Therefore, it is necessary to study the SO$_2$ corrosion resistance of catalysts applied to low temperature.

Compared with WO$_3$, MoO$_3$ is less affected by SO$_2$ and the chemical properties of MoO$_3$ are similar to those of WO$_3$. Kwon, D.W. et al. [49] have used ammonium molybdate (NH$_4$)$_2$MoO$_4$ and ammonium heptamolybdate (NH$_4$)$_2$Mo$_2$O$_7$ as precursors of molybdenum sources, and ammonium metatungstate hydrates as precursors for tungsten sources, compared with WO$_3$ and MoO$_3$ properties, to study MoO$_3$'s ability of resisting SO$_2$. The catalyst was characterized by X-ray photoelectron spectroscopy (XPS) analysis, and the results showed that the binding energy of ammonium heptamolybdate was higher than that of ammonium molybdate. High binding energy can promote the interaction of metal atoms and oxygen, which is beneficial to the redox and SCR reactions of NO$_x$. Furthermore, the Mo^{6+}/Mo^{5+} of ammonium heptamolybdate is higher than that of ammonium molybdate. The presence of Mo^{6+} on the surface of the catalyst can inhibit the reaction between SO$_2$ and V=O, reduce the absorption of SO$_2$, and thus play the role of resisting SO$_2$. Therefore, high Mo^{6+}/Mo^{5+} exhibits excellent resistance to SO$_2$. Figure 9 shows relative activity in the presence of SO$_2$ for the SCR of NO by NH$_3$ over different catalysts at 250 °C. It can be seen that the SO$_2$ has a certain effect on the catalyst. However, compared to the V$_2$O$_5$/TiO$_2$ and the V$_2$O$_5$/WO$_3$ system, the time for V$_2$O$_5$/MoO$_3$ to remain active is more prolonged. That is, V$_2$O$_5$/MoO$_3$ is more resistant to SO$_2$.
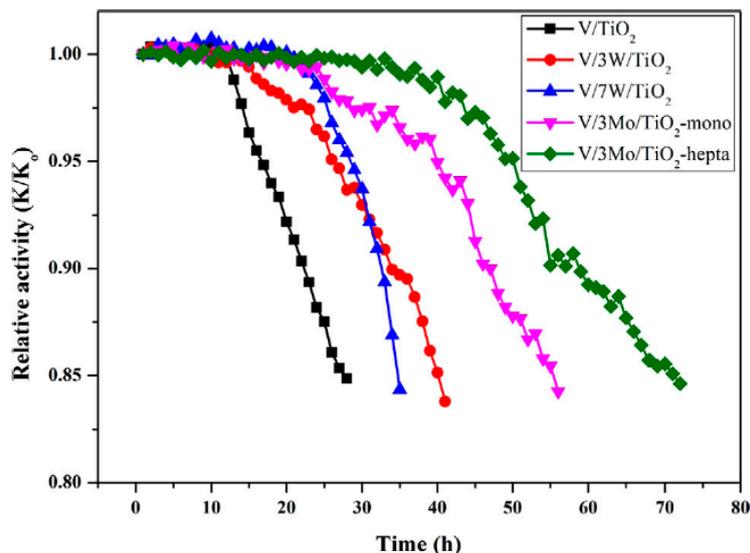
Figure 9. Relative activity in the presence of SO_2 for the SCR of NO by NH_3 over V/TiO_2, $V/3W/TiO_2$, V–$3Mo/TiO_2$-mono and $V/3Mo/TiO_2$-hepta at 250 °C. Reproduced with permission [49]. Copyright 2016, Elsevier.

It is important to note that, when testing against SO_2 toxicity, the controlled erosion conditions are only SO_2. However, in practical applications, the emitted gas may contain a certain amount of water vapor. At this point, SO_2 and H_2O, NH_3 more easily form ammonium sulfate on the surface of the catalyst to deactivate the catalyst. Generally, at temperatures between 200 and 300 °C, vanadium-based catalyst SCR reactions are strongly affected by coordination of water. The adsorbed ammonia on oxo vanadia Lewis acid sites and ammonium ions associated with Brønsted acid sites selective reduce weakly adsorbed NO via the E-R mechanism, and the water appears to shift the equilibrium between NH_3 and NH_4^+. At this time, the ratio between Lewis acid, Brønsted acid sites and V=O sites depend on the content of water vapor [15]. Because of the low SO_2 resistance of V_2O_5-WO_3/TiO_2, there are experiments showing that selecting Ce to replace V and the prepared $Ce_{0.2}W_{0.2}TiOx$ has good NOx conversion activity and N_2 selectivity [42]. The activity of the catalyst was stable under the condition of SO_2 only, while the decrease of the activity of the catalyst was observed under the condition of both SO_2 and H_2O. In addition, the performance of the Fe_1V_1/TiO_2 catalyst was tested with an aqueous test and anhydrous test, as shown in Figure 10, and the results showed that the activity in the anhydrous test was obviously better than that of the water test [17]. Based on this, it is necessary to discharge the prior drying or improve the resistance of the catalyst to water erosion performance.
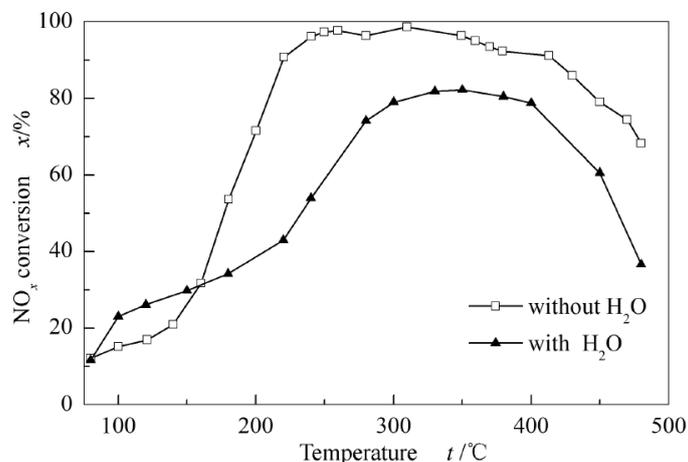

Figure 10. The effect of water vapor on NO_x conversion of Fe_1V_1/TiO_2 catalyst [17].

In addition, the actual application of high-temperature exhaust gas may be in some alkaline environment, and the catalyst may suffer alkali poisoning. Chen, L. et al. [50] have investigated the effects that alkali metals and alkaline earth metals may have on catalysts. It was found that the degree of poisoning of the catalyst increased with the increase of alkalinity, and the N_2O conversion rate decreased with the increase of alkaline content. The toxic element occupies the non-atomic pore site of the V_2O_5 [010] plane, so that the Brønsted acid and V^{5+}=O sites are blocked. In alkali metals such as Na, K will reduce the stability of Brønsted acid sites, reduce the absorption of ammonia, and reduce the amount of surface chemically adsorbed oxygen. By contrast, the effect of alkaline earth metals such as Ca and Mg on the reducibility of V is not obvious. Hu, W. et al. [51] have prepared V-Ce$(SO_4)_2$/Ti catalysts, utilizing the high oxygen storage ability and strong redox ability of Ce, and sulfate SO_4^{2-} that can increase surface acidity to obtain better performance by synergizing Ce with SO_4^{2-}. Ce introduces a high proportion of surface-active oxygen to increase the redox capacity of the catalyst. The abundant NO^+ and NO^{3-} on the surface form a redox cycle. The catalyst has better resistance to SO_2, H_2O, and alkali metal than the vanadium-based commercial catalyst. Gao et al. [52] used sulfided zirconia as a catalyst support and added Ce:V = 1:1 to obtain a CeVSZ(x) catalyst. The support provides too many acidic sites to react with the alkali metal and delay the acidity reduction. V partially replaces Ce to form $CeVO_4$, avoiding CeO_2 from being converted into $Ce_2(SO_4)_3$ to make it permanently inactivated. The CeVSZ(x) catalyst can maintain activity higher than 97% in the atmosphere of SO_2 and K coexistence, and there is no significant decrease in activity within 400 min. Huang, Z. et al. [53] prepared a hexagonal structure of WO_3 (HWO) as a support to load V_2O_5. The corner-sharing WO_6 octahedra form hexagonal tunnels oriented along the C-axis with space group P6/mmm, and the external surface of HWO allows V_2O_5 to be highly dispersed. The tunnels have relatively smooth surfaces and suitable sizes for alkalis' trapping specifically. Alkalis are readily inserted into tunnels by ion exchange reaction, so HWO has excellent resistance to alkali metal erosion. Figure 11 shows the catalytic activity evaluation of the V_2O_5/HWO catalyst and the V_2O_5/WO_3-TiO_2 catalyst at 350 °C under a gas containing NO, NH_3, SO_2 and alkali metal particles. It can be seen that the activity of V_2O_5/HWO is much higher than that of V_2O_5/WO_3-TiO_2 catalysts under the coexistence of SO_2 and alkali metal.
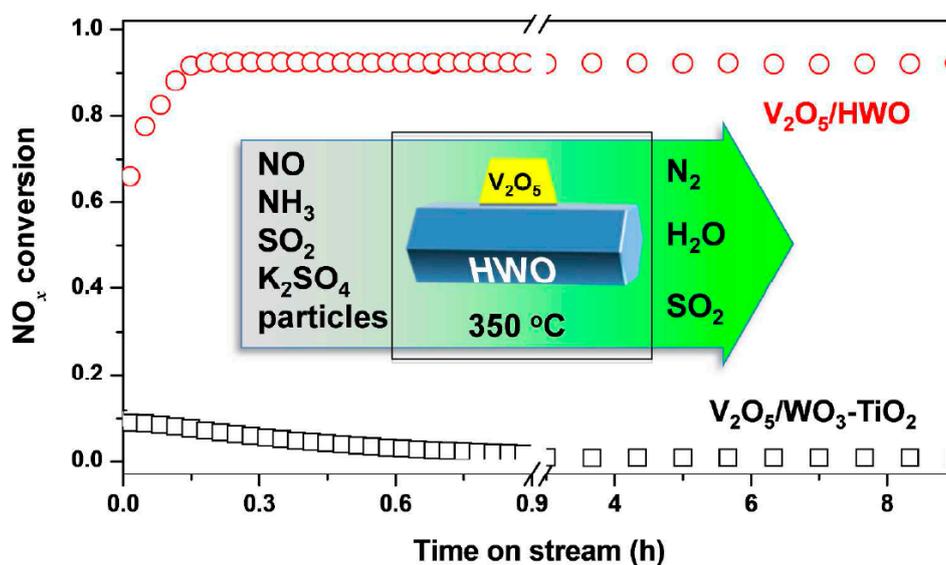
Figure 11. Activity evaluation of V_2O_5/HWO catalyst and V_2O_5/WO_3-TiO_2 catalyst at 350 °C. Reproduced with permission [53]. Copyright 2015, American Chemical Society.

5. Conclusions and Perspective

The vanadium-based catalyst is the most mature catalyst, and has a high catalytic activity at medium temperatures. However, considering the thermal instability of vanadium, the low-temperature

catalytic demand, and severe working environment in industrial production, the improvement of vanadium-based catalysts has become a research hotspot. The most common improvement method is in the modification of vanadium-based catalysts. Four major systems of cerium, iron, copper and manganese are widely used in this field. Cerium has excellent ability to store and release oxygen. The redox cycle is realized by Ce^{3+}/Ce^{4+} electron pairs, which provide oxygen vacancy and active sites and enhance the activity of catalysts. $CeVO_4$ stabilizes the surface V^{5+} species, accelerates redox cycle and NO_2 production, and helps to spur fast SCR. The cooperative effect between Ce and V leads to the enhancement of SCR activity. The presence of Ce^{3+}/Ce^{4+} increases surface chemisorbed oxygen and provide more acid sites. $CeVO_4$ promotes the formation of Brønsted acid sites while VO_x and CeO_2 provide Lewis acid sites on the surface. In addition, the Lewis acid sites may be converted to the Brønsted acid sites at high temperature SCR reactions. However, Ce is prone to generate $Ce_2(SO_4)_3$ with sulfate to cause permanent deactivation of the catalyst. At low temperatures, the unrivaled, high-activity of manganese-based oxides and copper-based oxides can significantly broaden the temperature window of vanadium-based catalysts, though they have poor low-temperature erosion resistance. The redox cycle ($V^{4+} + Mn^{4+} \leftrightarrow V^{5+} + Mn^{3+}$) reduces the energy required for electron transfer between Mn and V active sites, and promotes the adsorption and activation of NH_3 and NO. Mn^{3+} is conducive to NH_3-SCR reactions because it induces the formation of more surface chemisorbed oxygen. By introducing copper species, strong acid sites are increased. It is worth noting that Lewis acid sites are the strong acid sites in Cu-V/TiO_2 catalysts. Iron is cheap and nontoxic material with high hydrothermal stability. Due to the presence of Fe^{3+}-O-V^{5+} linkages, $FeVO_4$ incorporate a lot of surface defects which can adsorb or activate reactants. The adsorbed NH_3 prefers to be activated by Fe^{3+} due to the rapid electron transfer. The presence of electronic inductive effect between Fe^{3+} and V^{5+} was beneficial for high $deNO_x$ efficiency and N_2 selectivity. The VO_x species, the decomposition product of $FeVO_4$, exhibits higher SCR activity as active component. The presence of iron can be useful by altering the electron density of the VO_x surface species and inducing more Lewis acid sites and Brønsted acid sites for SCR reactions.

Although the research on denitrification catalysts has attracted widespread attention, the mechanism of SCR reaction is not yet clear. Research on the resistance of SO_2, H_2O, and alkali metals has made some progress, but there is still a lack of research on its inhibition mechanism. With the increasing importance of environmental protection, the development of vanadium-based catalysts is a general trend. Further study is expected to realize on the catalysis mechanism of synergistic effect and the performance optimization.

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