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Theory and practice of metal oxide catalyst design for the selective catalytic reduction of NO_x with NH_3

Wenpo Shan^a, Yunbo Yu^{a,b,c}, Yan Zhang^a, Guangzhi He^b, Yue Peng^d, Junhua Li^d, Hong He^{a,b,c,*}

^a Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

^b State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing

100085, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

^d School of Environment, Tsinghua University, Beijing 100084, China

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ABSTRACT

For NO_x control in the presence of excess oxygen, selective catalytic reduction with ammonia (NH_3 -SCR) has been successfully applied in the purification of coal-fired flue gas and diesel vehicle exhaust on a large scale. For both cases, various NH_3 -SCR catalysts have been developed, with the incorporation of desirable catalytic properties being the central issue. However, the fundamental principle for designing NH_3 -SCR catalysts with high activity, selectivity, and stability remain unclear. Generally, in the NH_3 -SCR reaction, the redox and acid sites on the catalyst are prerequisites that need to work together. Therefore, the close coupling of these dual functional sites is imperative for the design of NH_3 -SCR catalysts with high NO_x removal efficiency. Taking this intrinsic principle into account, we successfully designed and developed various novel catalysts with excellent NH_3 -SCR performance. This review will focus on the theory and practice of designing metal oxide catalysts for NH_3 -SCR.

1. Introduction

Nitrogen oxides (NO_x) play key roles in atmospheric chemistry and can induce the formation of photochemical smog, haze, and acid rain. Man-made NO_x emissions are primarily produced during combustion processes from stationary sources such as coal-fired power plants and mobile sources such as motor vehicles. With rapid industrialization and urbanization in the recent decades, increasing fossil fuel consumption has led to severe air pollution worldwide, especially in China, with its air pollution attracting global attention. Regional air pollution complexes, combined with coal-combustion and vehicle-exhaust pollution, have emerged in key city clusters of China, with haze and photochemical pollution frequently appearing in winter and summer, respectively. Due to its crucial contribution to the formation of haze and photochemical smog, the control of NO_x emissions is of great importance for the overall improvement of ambient air quality.

The catalytic purification of NO_x emissions from stationary sources and diesel engines is essential [1–3]. In both cases, the common presence of excess oxygen, water vapor, and sulfur oxides provide difficult conditions for NO_x removal. Selective catalytic reduction of NO_x with ammonia/urea (NH₃-SCR) is the dominant technology for NO_x control and has been successfully applied for the purification of coal-fired flue gas and diesel vehicle exhaust on a large scale. However, to meet the increasingly stringent emission regulations, serious issues still need to be resolved for NH₃-SCR technology.

Research on NH₃-SCR has increased in recent years, with the related catalysts playing key roles in the development of this technology. Metal oxides with variable valence are active in NH₃-SCR. Therefore, various metal oxides with different properties, such as V, Mn, Fe, Ce-based oxides, have been developed for the control of NO_x emissions from different sources over the past several decades [2,4]. Various metal-exchanged zeolites, such as Fe or Cu exchanged ZSM-5, SSZ-13, or SAPO-34, have also been developed for application in diesel vehicles due to their hydrothermal properties. Several papers have comprehensively reviewed research progress on zeolite catalysts for NH₃-SCR [5–7]. Therefore, the current review will focus on metal oxide catalysts, which have been widely applied in industries for the removal of NO_x from both stationary and mobile sources.

E-mail address: honghe@rcees.ac.cn (H. He).

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^{*} Corresponding author at: Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.

The chemical and mechanistic aspects of NH₃-SCR on metal oxide catalysts were comprehensively reviewed 20 years ago, with catalytic systems based on supported V₂O₅ and catalysts containing Fe₂O₃, CuO, MnO_x , or CrO_x discussed [2]. After that, some review papers focused on V-based catalysts [8], V-free catalysts [4], Ce-based catalysts [9], and Mn-based catalysts [10], respectively, were published. In addition, the low-temperature performance and poisoning resistance of NH₃-SCR catalysts were particularly reviewed [11-13]. However, an overview of different types of metal oxide catalysts that connect the structure-activity relationships and reaction mechanisms with catalyst design and a summary of the universal principle for high performance catalysts for NH₃-SCR are yet to be reported. To fill these gaps and guide catalyst development and improvement, this review will focus on the theory and practice of metal oxide catalyst design for NH3-SCR and establish fundamental principle for catalyst design.

2. Key reactions of NH₃-SCR

The primary pollutant of NO_x directly emitted from combustion processes is NO, together with a small proportion of NO₂. Therefore, the main reaction under NH₃-SCR conditions is the standard SCR reaction (reaction 1):

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

In this reaction, the two N atoms in the formed N₂ are due to a coupling of one nitrogen atom from NO and one from NH₃ [2]. When half of the NO_x consists of NO₂, the conversion of NO_x is remarkably enhanced, especially at low temperatures, due to the fast SCR reaction (reaction 2):

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{2}$$

To obtain high NO_x conversion, NO is sometimes partially preoxidized to NO_2 before NH_3 -SCR; for example, by diesel oxidation catalyst (DOC) for diesel vehicles.

In addition to the standard and fast SCR reactions, several side reactions also occur simultaneously. In low-temperature regions, NH_4NO_3 may accumulate through reaction 3:

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \tag{3}$$

In high-temperature regions, the non-selective catalytic reduction (reaction 4) and catalytic oxidation of NH_3 (reactions 5 and 6) will occur:

 $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$ (4)

 $4\mathrm{NH}_3 + 5\mathrm{O}_2 \rightarrow 4\mathrm{NO} + 6\mathrm{H}_2\mathrm{O} \tag{5}$

$$4\mathrm{NH}_3 + 7\mathrm{O}_2 \rightarrow 4\mathrm{NO}_2 + 6\mathrm{H}_2\mathrm{O} \tag{6}$$

Reactions 4–6 favor the formation of N₂O, NO, and NO₂, respectively, which reduces N₂ selectivity and NO_x conversion [14]. Therefore, the development of NH₃-SCR catalysts with good performance needs to promote reactions 1 and 2 while inhibiting reactions 4–6 (Fig. 1).

3. Metal oxide catalysts for NH₃-SCR

3.1. Vanadia-based oxide catalysts

Vanadia-based oxide catalysts, especially WO₃- or MoO₃-doped V₂O₅/TiO₂, with excellent SO₂ resistibility, have been widely used for the removal of NO_x generated from stationary sources since the 1970s [2]. With proper modification of catalytic properties, vanadia-based catalysts have also been used for the SCR of NO_x from diesel engines [1,15].



Fig. 1. Key reactions of NH₃-SCR.

[8]. The typical compositions of this catalyst and main functions of each component are shown in Fig. 2. V2O5 is very active for NH3-SCR reactions due to its redox properties and acidity, with the vanadia species in the V^{5+} oxidation state as active sites for $\rm NH_3\text{-}SCR$ reaction [8,16]. In addition, it is an industrial catalyst for oxidizing SO₂ to SO₃ in sulfuric acid production. Therefore, V₂O₅ has an extraordinary inherent resistibility to sulfur poisoning in the NH3-SCR reaction. During the development of vanadia-based catalysts, various metal oxides, such as Al₂O₃, SiO₂, ZrO₂, and TiO₂, have been tried as the support, with anatase TiO₂ finally selected. The low decomposition temperature of titanium sulfate endues TiO₂ with inherent resistibility to sulfur poisoning. Previous studies have also indicated that anatase TiO₂ is favorable for good dispersion of active V2O5 and can supply acid sites for NH3-SCR reactions [2]. The addition of MoO₃ can inhibit the poisoning effects of As compounds [2]. The WO_3 can act as a structural promoter to inhibit the phase transformation of anatase TiO₂, which is favorable for the improvement of thermal stability [8]. It can also act as a chemical promoter to increase surface acid sites, which helps inhibit the over oxidation of NH₃ and undesired oxidation of SO₂, and thereby enhances high-temperature NO_x conversion, N_2 selectivity, and SO_2 resistance [17].

To promote the performance of traditional vanadia-based catalysts, many studies have attempted to improve the catalyst from the aspects of preparation method, support, and promoter, resulting in the development of various catalysts, including V₂O₅/TiO₂-PILC [18,19], V₂O₅/microporous TiO₂ [20], V₂O₅/TiO₂-SiO₂ [21], V₂O₅-WO₃-TiO₂--SiO₂ [22], V₂O₅/Ce_{1-x}Ti_xO₂ [23], V₂O₅/AC [24], and V₂O₅/CNTs [25]. The coupling of V₂O₅ with a secondary metal species with good redox



Fig. 2. Typical compositions of industrial vanadia-based catalyst and the main functions of each component.

properties (such as Fe, Ce, Mn, and Cu) has also been investigated to obtain catalysts with dual redox functions, such as FeVO₄ [26], FeVO₄/TiO₂ [27], FeVO₄/TiO₂-WO₃-SiO₂ [28], CeVO₄ [29], CeVO₄/-TiO₂ [30], Zr-promoted CeVO₄ [31], W-promoted CeVO₄ [32], MnO_x--V₂O₅/TiO₂ [33], CuO-V₂O₅/WO₃-TiO₂ [34], and Sb-promoted Cu₃V₂O₈/TiO₂ [35]. These improvements were mainly associated with the tuning of the acidic and/or redox functions of the catalyst. Most of these modified catalysts were developed for the control of NO_x emissions from stationary sources and targeted the enhancement of low-temperature performance and resistance to poisoning effects. On the other hand, the improvement of vanadia-based catalyst for application on diesel vehicles mainly aims to enhance the thermal stability and widen the temperature window.

Although high V₂O₅ loading may result in high activity, high V₂O₅ content can simultaneously decrease thermal stability and N₂ selectivity and facilitate the catalytic oxidation of SO_2 to SO_3 [2,21]. The formation of SO₃ can induce severe problems for equipment due to corrosion and for the catalyst due to ammonium bisulfate (ABS) blocking. Therefore, the development of an active vanadia-based catalyst with low V₂O₅ loading is crucial. With experimental and computational studies, it was found that polymeric vanadyl species possess much higher NH₃-SCR activity than monomeric vanadyl species [8,36,37]. Thus, polymeric vanadyl species, rather than monomeric vanadyl species, determined NH₃-SCR performance under low-temperature conditions. The polymerization of vanadyl species can be enhanced by the introduction of sulfate, thereby obtaining low-vanadia catalyst with excellent low-temperature performance [37,38]. It has been reported that, both VO_x and WO_x components are almost exclusively segregated to the surface of the TiO₂ support upon calcination of the V₂O₅-WO₃/TiO₂ catalyst, and thus WO_x can facilitate the polymerization of VO_x and enhance NH₃-SCR performance as well [8,39]. Based on these previous fundamental results, we successfully realized the industrialization of the designed vanadia-based catalyst for diesel vehicles [40]. These SCR catalytic converters can meet the China IV and V standards for diesel vehicles and have been applied widely for heavy-duty diesel vehicles.

Although vanadia-based catalysts have been applied for 40 years, several issues remain with this type of catalyst, such as the toxicity of active vanadium species, narrow temperature window, and low thermal stability (Fig. 3). Therefore, great efforts have been made on the development of vanadium-free oxide catalysts for NH_3 -SCR in the last decades [4].

3.2. Vanadium-free oxide catalysts

Variable-valence metal oxides are generally active in NH₃-SCR. Mn-,

Fe-, and Ce-based oxides are three representative types of vanadium-free oxide catalysts those have attracted most attentions [4,9,10]. To enhance catalytic performance, acid metal oxides, such as TiO_2 , WO_3 and MOO_3 , can be coupled with variable-valence metal oxides (Fig. 4).

3.2.1. Mn-based oxide catalysts

With the wide application of NH₃-SCR in coal-fired power plants, the control of NO_x emissions from non-electric industries has become increasingly important. For example, NO_x emissions from electrical power plants decreased by 81.1 % due to the application of NH₃-SCR during the 12th Five-Year Plan period (2010–2015) in China. However, considerable challenges remain for the control of NO_x emissions from coking, iron and steel metallurgy, cement, ceramics, and industrial boilers. Flue gas from non-electric industries is characterized by low temperature (120–300 °C); as such, the traditional medium temperature (300–400 °C) for NH₃-SCR catalysts in power plants cannot be directly used. Therefore, substantial efforts have been made to develop NH₃-SCR catalysts with good performance in the low-temperature range.

In addition to improvement of vanadia-based catalysts, Mn oxides, with unique redox functions, have attracted substantial attention for the control of NO_x from industrial flue gas [41,42]. Pure MnO_x possesses prominent low-temperature performance, with 100 % NO_x conversion even achieved at \leq 100 °C under extremely high space velocity of 700, 000 h⁻¹ [43]. Different preparation methods [43,44] and precipitants [45] have been used to prepare different types of MnO_x, with amorphous structure and high surface area found to be important for the excellent catalytic performance at low temperatures. However, the high redox property also induces some negative effects, such as high selectivity to



Fig. 4. Main compositions of vanadium-free oxide catalysts.



Fig. 3. The advantages / disadvantages of vanadia-based catalysts.

N₂O in NH₃-SCR reactions and narrow temperature window [14].

To improve NH₃-SCR performance, different types of supports have been used for Mn-based oxide catalysts, such as MnOx/TiO2 [46-48], MnOx/SiO2 [47], MnOx/Al2O3 [49], MnOx/AC [50], and MnOx/-CeO₂-ZrO₂-Al₂O₃ [51]. In addition, metal oxides with milder redox properties and/or metal oxides with higher acidity have been used to modify MnO_x, thus obtaining Mn-Fe/TiO₂ [52], Mn/Fe-Ti spinel [53], Mn-Ce/TiO₂ [54], Mn-Ni/TiO₂ [55], MnCoO_x [56,57], Mn-Ce oxide [58, 59], Mn-W oxide [60], Mn-Fe oxide [61], Mn-Zr oxide [62], and Mn-Cu oxide [63] with better activity, N2 selectivity, or poisoning resistance. During the last several decades, considerable efforts have been made to improve Mn-based catalysts for industrial application for low-temperature NH₃-SCR, although the poisoning effects of SO $_2$ remain a challenge. The formation of NH4HSO4 and (NH4)2SO4 can block surface active sites, and the sulfation of Mn can interrupt the redox cycle between Mn^{4+} and Mn^{3+} [10,42,64]. For the poisoning effects, S^{4+} of SO_2 needs to be transformed to S^{6+} . Therefore, it is important to depress the oxidation of SO₂ over the catalyst for the enhancement of sulfur resistance. At the same time, the NO oxidation capability needs to be maintained for the NH₃-SCR process. Thus, Mn-based oxide catalysts still need to be designed and modified under theory guidance.

3.2.2. Fe-based oxide catalysts

Fe-based oxides have been investigated as NH₃-SCR catalysts for several decades [4]. The catalytic performance of Fe₂O₃ can be enhanced by tuning the crystal phase and shape at the nanometer level [65]. More frequently and efficiently, Fe oxide is promoted by acidic oxides, such as TiO₂ and WO₃, and the obtained Fe-Ti oxide [66–69] and Fe-W oxide [70,71] catalysts usually possess high NO_x conversion, N₂ selectivity, and SO₂ durability in the medium temperature range. Some Fe-based oxides with more complex components have also been developed, such as Fe-TiO₂-PILC [72], Fe₂(SO₄)₃/TiO₂ [73], Fe-Ce-Ti oxides [74], Fe-Cu-Ti oxides [75], Fe-W-Ti oxides [76], Fe-W-Ce oxides [77], and Fe-W-Zr oxides [78,79].

To obtain high NH₃-SCR activity, we developed an FeTiO_x catalyst in which Fe and Ti oxides were combined at the atomic level by coprecipitation [68]. The FeTiO_x catalyst showed much better catalytic performance than the Fe₂O₃/TiO₂ catalyst prepared by impregnation (Fig. 5) [80]. Iron titanate crystallite with a specific Fe-O-Ti structure was reported to be the main active phase for the FeTiO_x catalyst, and the synergistic effects between iron and titanium (as acid sites) species at the atomic scale resulted in high activity. Based on systemic characterizations, including N₂ physisorption, XRD, XPS, H₂-TPR, UV–vis DRS, Raman spectroscopy, and XAFS, a specific edge-shared Fe³⁺-(O)₂-Ti⁴⁺

structure was proposed (Fig. 5) [81]. At low temperatures, NO is oxidized to nitrate species on Fe³⁺ (as redox sites) and then reacts with adjacent adsorbed NH₄⁺ species on Ti⁴⁺–OH Brønsted acid sites to form intermediate ammonium nitrate species, followed by the final reaction with gaseous NO to produce N₂ and H₂O [82]. At high temperatures, the adsorbed NH₃ species on Ti⁴⁺ can be activated to -NH₂ species by neighboring Fe³⁺ sites, and then react with gaseous NO to form a NH₂NO intermediate and finally decompose into N₂ and H₂O [82].

Very recently, a single-atom Mo/Fe₂O₃ catalyst was developed by anchoring single Mo ions on (001) surfaces of reducible α -Fe₂O₃, and the individual Mo ion and one neighboring Fe ion were thus constructed as one dinuclear site [83]. Since the Mo and Fe ions can provide acidic and redox functions, respectively, the dinuclear site acts as a highly active acid-redox site for NH₃-SCR.

3.2.3. Ce-based oxide catalysts

Due to its excellent oxygen release/storage properties, the rare-earth metal oxide ceria is widely used as a promoter to enhance performance of various catalysts [9,84]. For NH₃-SCR catalysts, ceria is also an effective promoter for vanadium-based catalysts [85], zeolite catalysts [86], and Mn-based low-temperature catalysts [54]. Ce oxide has excellent redox properties due to the redox shift between Ce^{3+} and Ce^{4+} . Through the combination of Ce with acidic components, we developed a Ce-based NH₃-SCR catalyst ten years ago, resulting in the preparation of a Ce-Ti oxide (Ce/TiO₂) catalyst by impregnation [87]. Ce oxide has since been widely used as the main active component in NH₃-SCR catalysts, and the study of Ce-based catalysts has become an important research area for NH₃-SCR [9].

Preparation methods play crucial roles in the determination of the interaction between the components of a catalyst, and thereby influence catalytic performance for NH₃-SCR. To improve the catalytic performance of Ce-Ti oxides, different preparation methods have been employed, such as sol-gel [88], co-precipitation [89], homogenous precipitation [90], flame-spray [91], and spontaneous deposition [92]. These methods produce catalysts with different structural properties and combination types of components. The Ce-O-Ti short-range order species with interaction between Ce and Ti at the atomic scale are proposed to be active sites [89]. Generally, to obtain highly efficient catalysts, the preparation process must achieve high dispersion of active CeO₂. Different promoters have been used to improve NH3-SCR activity, N2 selectivity, poisoning resistance, and thermal stability of Ce-Ti oxide catalysts [9]. As a result, Ce-Fe-Ti oxides [93], Ce-Cu-Ti oxides [94], Ce-Co-Ti oxides [95], Ce-Bi-Ti oxides [96], Ce-Sn-Ti oxides [97], Ce-W-Ti oxides [98,99], Ce-Mo-Ti oxides [100,101], Ce-Nb-Ti oxides



Fig. 5. Activity and microstructural model of Fe-Ti oxide catalyst [80,81]. Reaction conditions: $[NO] = [NH_3] = 500 \text{ ppm}$, $[O_2] = 5 \text{ vol.}\%$, N_2 balance, and $GHSV = 50,000 \text{ h}^{-1}$.

[102], Ce-Zr-Ti oxides [103,104], and Ce-Si-Ti oxides [105] have been developed. These added promoters mainly enhance the redox and acidic functions of the catalyst.

To improve surface acidity, different acids have been used to modify CeO₂. Sulfuric acid and phosphoric acid are very effective at improving the catalytic performance of CeO₂ [106–108]. Different metal oxides, such as the oxides of W [109-111], Mo [112], and Nb [113], have also been used to modify CeO₂ for NH₃-SCR. Among them, WO₃ with intense acidity is highly compatible for coupling with CeO₂, with the obtained Ce-W oxide catalysts presenting excellent NO_x conversion, N₂ selectivity, and poisoning resistance in a wide temperature range, even under high space velocity [109,110,114]. The synergistic interactions between well-dispersed Ce and W oxide phases, with CeO₂ acting as a redox site and WO3 acting as an acid site, are crucial for excellent catalytic performance [91,115]. With the close coupling of CeO₂ and WO₃, a CeWO_x catalyst prepared by homogenous precipitation exhibit much better catalytic performance than the industrially applied V2O5-WO3/TiO2 and Fe-ZSM-5 catalysts [109], and NH₃-SCR systems based on the CeWO_x catalyst ensure that the NO_x emissions from a heavy duty diesel engine meet the Euro V limit (Chinese V limit), without the need for any other aftertreatment device, in an engine bench test [116].

4. Reaction mechanism of NH₃-SCR

To gain insight into NH_3 -SCR reactions over metal oxide catalysts, extensive research has been devoted to the reaction mechanisms on different catalysts, such as the abovementioned V-based, Mn-based, Febased, and Ce-based catalysts, by various methods, such as spectroscopy, adsorption-desorption, kinetics, and computational studies [2,4,8, 117]. Different hypotheses have been proposed for different catalyst components, metal loadings, and test conditions.

A well-known catalytic cycle for the SCR reaction over V-based catalysts involving both acid-based and redox functions was proposed by Topsøe, which indicated that both redox and acid sites are needed for NH₃-SCR [118]. Redox functions and surface acid properties play key roles in NH₃-SCR performance at low and high temperatures, respectively [119]. Although significant progress has been achieved in regards to our understanding of NH₃-SCR reactions over V-based catalysts, debate remains for some issues, including the dominant role of isolated vs. oligomeric surface vanadia sites, importance of Brønsted vs. Lewis acid sites, and nature of surface reaction intermediate complexes [16,

120,121].

Based on DFT calculations and experimental evidence, we deduced the entire NH₃-SCR mechanism over monomeric and polymeric vanadia/TiO₂ surfaces (Fig. 6). The computational results showed that the coupling effect of the polymeric vanadyl species markedly reduced the overall reaction barrier of the catalytic cycle. Therefore, the dimeric vanadyl species, rather than the monomeric vanadyl species, determined the low-temperature performance of V-based catalysts for NH₃-SCR, being in consistent with the experimental results [36-38]. The requirement for redox and acid sites for NH3-SCR over V-based catalysts also accounts for vanadium-free oxide catalysts. For example, previous study has suggested that the NH3-SCR reaction mechanism for CeO2-WO3 catalysts consists of two independent cycles, i.e., a redox cycle due to the excellent oxygen storage capability and reducibility of CeO₂ and an acid site cycle resulting from Brønsted acid sites formed on the W-O-W species of Ce₂(WO₄)₃ [122]. In addition, an NH₃-SCR cycle pathway over β-MnO₂ catalysts has been reported on the basis of DFT calculations [43]. NH₃ tends to be adsorbed at the Lewis acid Mn site on MnO₂ surfaces. Adsorbed NH₃ is activated by the transfer of a H atom to surface lattice O and subsequently reacts with NO in the gas phase, resulting in the formation of an NH₂NO intermediate. NH₂NO is further changed into N₂ through dehydrogenation/hydrogenation. The rate-limiting step is the removal of surface H atoms. This reaction mechanism is somewhat similar to that proposed by us for the V-based catalyst system (Fig. 6).

Although there is still some debate on the reaction mechanisms of NH₃-SCR, it is well accepted that two types of reaction mechanisms exist for metal oxide catalysts, i.e., the Langmuir-Hinshelwood (L-H) mechanism (reaction between adsorbed NO_x and NH₃ species) at low temperature and Eley-Rideal (E-R) mechanism (reaction between adsorbed NH₃ species and gaseous NO) at high temperature. For example, the NH_3 -SCR mechanisms for FeTiO_x catalysts with a specific Fe-O-Ti structure at different temperature ranges have been proposed (Fig. 7) [82]. Both Brønsted and Lewis acid sites are involved in the reaction. NH₃ is mainly adsorbed on Ti sites in the form of ionic NH⁺₄ and coordinated NH₃, whereas NO_x is mainly adsorbed on Fe sites in the form of monodentate nitrate. At low temperatures (<200 °C), the reactive surface species are mainly NH₄⁺ and monodentate nitrate, and the reaction mainly follows the L-H mechanism, in which the formation of monodentate nitrate from NO oxidation by O2 over Fe3+ is the rate-determining step. On the other hand, at high temperatures



Fig. 6. Mechanism of standard NH_3 -SCR reaction. (A) Reactions over monomeric V_2O_5/TiO_2 surfaces. (B) Reactions over dimeric V_2O_5/TiO_2 surfaces. Reactants are marked in red; products are marked in blue [37] (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 7. Proposed NH_3 -SCR reaction mechanisms over $FeTiO_x$ catalysts at different temperature ranges [82].

(>200 °C), the reaction mainly follows the E–R mechanism, in which the formation of NH₂NO intermediate species following H-abstraction of NH₃ by neighboring Fe³⁺ is the rate-determining step.

Based on the NH₃-SCR reaction mechanisms over metal oxide catalysts, it can be concluded that the key points for the adjustments of low-temperature and high-temperature performances are redox functions and acid properties, respectively.

The deactivations induced by chemical poisons, such as alkali/ alkaline earth metals and SO₂, are important issues for NH₃-SCR catalysts. The deactivation effects of alkali/alkaline earth metals on NH₃-SCR catalysts are attributed to the decrease of surface acidity and reducibility, which are the key for the adsorption and activation of NH₃ and NO_x [123–125]. The formation of metal sulfates, due to the exist of SO₂, can induce irreversible poisoning effects owing to the loss of redox functions and the cutoff of L-H reaction pathway [12,126–129]. In addition, thermal aging can also induce decline of redox ability and surface acidity for NH₃-SCR catalysts, as well as segregation of redox and acid sites, and thus results in deactivations [91,130–132]. Therefore, the stabilization of redox and acid sites is the key to design NH₃-SCR catalysts with good poisoning resistance and high thermal stability.

5. Design principle and applications of NH₃-SCR oxide catalysts

In recent years, considerable efforts have been devoted to the development of environmentally benign, highly efficient, and thermally stable NH_3 -SCR catalysts. However, theoretical guidance for the development of a highly efficient NH_3 -SCR catalyst is still lacking, and design principle for NH_3 -SCR catalysts is urgently required. Based on extensive understanding of the structure-activity relationship of NH_3 -SCR catalysts and the reaction mechanism at different temperature ranges, we established a high dispersion-close coupling (HDCC) principle for the design of NH_3 -SCR catalysts that involves the close coupling of redox and acid sites, thus guiding the development of mixed oxide catalysts with excellent performance.

The NH_3 -SCR reaction is determined by the redox properties of the catalyst. Thus, we propose that metal oxides with variable valence are active in NH_3 -SCR and V-, Mn-, Fe-, and Ce-based oxides can exhibit

good NH₃-SCR performance. On the other hand, an acid component is needed to guarantee the occurrence of the reaction. In the NH₃-SCR reaction, the redox and acid sites must work together. Therefore, high dispersion of sites with the same function and close coupling of sites with different functions are key factors for the design of a highly efficient NH₃-SCR catalyst (Fig. 8).

Using the variable-valence metals V, Fe, Ce, and Mn as redox components, and Ti, W, and Mo as acid components, we closely coupled the two types of components with a short-range ordered and highly dispersed structure. Thereby, novel V-S-Ti [37], V-Nb-Ce [133], Fe-Ti [80], Fe-Mn-Ti [134], Fe-W [71], Mn-W [60], Mn-Nb [135], Ce-Ti [136], Ce-W-Ti [99], Ce-W [109], Ce-Nb [137], Ce-W-Zr [138], and Ce-Mo-Zr [139] oxide catalysts with excellent NH₃-SCR performance were developed. These achievements provide a theoretical basis and practical examples for the development of novel and highly efficient NH₃-SCR catalysts.

To explain the application of the design principle for highly efficient NH₃-SCR catalysts, the development of Ce-based catalysts under theoretical guidance was used as an example (Fig. 9).

Through the combination of redox and acidic components, a Ce/TiO2



Fig. 8. Design principle of NH₃-SCR oxide catalysts.



Fig. 9. Development of Ce-based catalysts under guidance of design principle [87,99,134]. Reaction conditions: $[NO] = [NH_3] = 500 \text{ ppm}, [O_2] = 5 \text{ vol.\%}, N_2 \text{ balance, and GHSV} = 100,000 \text{ h}^{-1}.$

catalyst was firstly prepared by an impregnation method [87]. Both the pure ceria and titanium dioxide showed rather poor SCR performance in the whole temperature range, whereas the Ce/TiO₂ catalyst showed good performance over a relatively wide temperature range, indicating the synergistic effects between the redox component of ceria and acidic component of titanium dioxide due to the formation of active Ce-O-Ti species [89].

For the purpose of enhancing the coupling degree of cerium and titanium oxides, the preparation method was improved. The catalyst prepared by impregnation showed clear phase separation, whereas homogenous precipitation was able to closely couple the cerium and titanium oxides [134]. Therefore, the catalyst prepared by homogenous precipitation exhibited enhanced SCR activity.

To further improve the catalytic performance, tungsten was used as a catalyst promoter [99]. The addition of tungsten enhanced the dispersion of surface cerium and the formation of surface oxygen vacancies, and thereby improved low-temperature performance due to enhanced redox functions. On the other hand, the addition of tungsten enhanced the adsorption of NH₃ and inhibited the unselective oxidation of NH₃ due to its strong acidity and weak oxidizability, and thus high-temperature NO_x conversion and N₂ selectivity were both improved.

6. Summary and outlook

Research on NH₃-SCR catalysts and reactions has attracted great interest worldwide, especially in recent years due to the increasingly stringent standards for NO_x emissions. Metal oxides with variable valence are generally active in NH₃-SCR. Various NH₃-SCR catalysts with different properties have been developed for the control of NO_x emissions from different sources over the past few decades, including V-, Mn-, Fe-, and Ce-based oxides with high NH₃-SCR activity. Based on extensive understanding of the structure-activity relationship of NH₃-SCR catalysts and the reaction mechanism at different temperature ranges, we established a principle for the design of NH₃-SCR catalysts to guide the development of mixed oxide catalysts with excellent performance. In the NH₃-SCR reaction, the redox and acid sites must work together. Therefore, high dispersion of sites with the same function and close coupling of sites with different functions are key factors for the design of a highly efficient NH₃-SCR catalyst.

Due to the urgent demand for NO_x control in the non-electric industry, the development of NH_3 -SCR catalysts with good performance at low-temperature range, together with resistance to the poisoning effects of SO₂, H₂O, and alkaline particulates, is crucial for denitration from stationary sources. Low-temperature performance is also very important for diesel vehicles to meet the increasingly stringent standards for NO_x emissions. There are limitations in regard to the catalyst volume that can be placed on board, which requires that the catalyst works efficiently for NH₃-SCR. In addition, the hydrothermal stability of catalysts on diesel vehicles is of great importance due to the combining of SCR with DPF (diesel particulate filter).

Although various metal oxides have been investigated for NH_3 -SCR over the past several decades, there are still many challenges in this area. For low-temperature NO_x abatement from flue gas, the SCR performance of traditional vanadia-based catalysts needs to be enhanced together with depression of SO_2 oxidation activity, and the resistance of Mn-based oxide catalysts to SO_2 poisoning needs to be substantially improved. Improvement of hydrothermal stability is also required for V-, Fe-, and Ce-based oxides catalysts, which is a primary factor restricting their practical application in diesel vehicles.

Under the guidance of the HDCC design principle, close coupling of the redox and acid sites is a key factor for the design of highly efficient NH_3 -SCR catalysts. The balance and stabilization of redox and acid functions are also key for the improvement of poisoning resistance, N_2 selectivity, and thermal stability of NH_3 -SCR catalysts. In addition, enhancing our fundamental understanding of the structure-activity relationships and the NH_3 -SCR reaction mechanisms is important for improving catalyst design theory.

Declaration of competing interest

None.

CRediT authorship contribution statement

Wenpo Shan: Writing - original draft, Writing - review & editing, Funding acquisition. Yunbo Yu: Writing - review & editing. Yan Zhang: Writing - review & editing. Guangzhi He: Writing - review & editing. Yue Peng: Writing - review & editing. Junhua Li: Writing - review & editing. Hong He: Conceptualization, Writing - review & editing, Funding acquisition.

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