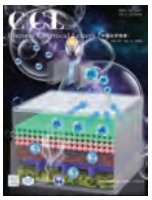
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Iron-based catalysts for NO_x reduction: Reaction mechanism and anti-poisoning strategies

Zaisheng Jin[a,1], Fuli Wang[a,1], Yongjie Shen[a,b], Xiaonan Hu[a], Yanqi Chen[a], Jin Zhang[a], Ming Xie[c], Penglu Wang[a,*], Dengsong Zhang[a,*]

[a] International Joint Laboratory of Catalytic Chemistry, State Key Laboratory of Advanced Special Steel, Innovation Institute of Carbon Neutrality, Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, China
[b] Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 001-0021, Japan
[c] Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

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ABSTRACT

Iron-based metal oxide catalysts are widely used for selective catalytic reduction (SCR) of NO_x with NH_3 due to their excellent catalytic performance at medium and high temperatures, high nitrogen selectivity, robust resistance to sulfur dioxide poisoning, environmental sustainability and cost effectiveness. However, several challenges including sub-optimal low-temperature catalytic activity, narrow operating temperature range, poor resistance to alkali/alkaline earth metal poisoning, as well as insufficient thermal stability and H_2O/SO_2 resistance always hinder the further application of iron-based metal oxide catalysts, which is in urgent need of further improvement in practical applications. This review provides a comprehensive overview of the development, applications and challenges associated with different types of iron-based metal oxide catalysts and suggests corresponding modification strategies to address the as-mentioned issues. Iron oxide catalysts can promote low-temperature catalytic performance by adjusting crystal structures and exposing specific crystal faces; however, their thermal stability and resistance to SO_2/H_2O and alkali metals still have substantial room for improvement. Iron-based composite metal oxide catalysts can effectively increase the resistance to SO_2/H_2O by coupling multiple metals and modulating adjacent electronic sites. Iron-based acidic salt catalysts greatly enhance the resistance to alkali metal poisoning by enriching the surface acid sites and providing sacrificial sites. Supported iron-based metal oxide catalysts can significantly improve both catalytic performance and resistance by modulating reaction pathways and constructing core-shell structures. This review clarifies the important direction of further research on iron-based metal oxide catalysts, and provides scientific basis and design ideas for the development and application of high-efficiency low-temperature NO_x reduction catalysts.

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1. Introduction

Nitrogen oxides (NO_x), as one kind of main atmospheric pollutants, have contributed to numerous environmental problems, including acid rain, photochemical smog, and haze. Selective catalytic reduction (SCR) is the most effective technique for controlling NO_x emissions from both stationary and mobile sources and has been widely applied. As the key to this technique, the research and development of NH_3-SCR catalysts with excellent performance has attracted continuous attention from researchers all over the world. The V_2O_5-WO_3/TiO_2 catalyst currently used in commercial applications exhibits high efficiency in the SCR reaction. However, the inherent toxicity of V_2O_5 and relatively narrow operating temperature window limit its broader use [1,2]. As an alternative to the V_2O_5-WO_3/TiO_2 system, iron-based catalysts have become one of the hottest spot research due to their satisfied medium and high temperature activity, high N_2 selectivity, strong resistance to SO_2 poisoning, environmental friendliness and low price. Iron-based catalysts are generally divided into iron-based zeolite catalysts and iron-based metal oxide catalysts. Compared to iron-based zeolite catalysts, iron-based metal oxide catalysts exhibit superior low temperature activity and sulfur resistance [3,4]. In general, iron-based metal oxide catalysts mainly include bulk iron oxides catalysts (*i.e.*, iron oxide and iron-based/iron-containing composite oxides), iron-based acidic salt catalysts and supported iron-based catalysts.

* Corresponding authors.
E-mail addresses: plwang@shu.edu.cn (P. Wang), dszhang@shu.edu.cn (D. Zhang).
[1] These authors contributed equally to this work.

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Pure Fe_2O_3 exhibits excellent NH_3-SCR catalytic performance, which is closely linked to its morphology and structural properties [5]. As active components or additives in NH_3-SCR catalysts, FeO_x can improve both catalytic activity and resistance to sulfur dioxide poisoning. Wang *et al.* [6] demonstrated that the formation of a Fe-O-Ce solid solution structure by doping Fe into CeO_2 reduced the activation energy and improved the redox performance. Liu *et al.* [7] proposed the introduction of WO_3 into Fe_2O_3 enabled the catalyst to maintain optimal redox performance, effectively reducing the non-selective catalytic oxidation of NH_3, thereby improving NH_3-SCR performance. Wu *et al.* [8] reported the preparation of Mn-Fe-Ti mixed oxide catalysts *via* CTAB-assisted coprecipitation, which exhibited enhanced resistance to H_2O/SO_2 due to strong electronic interactions and high dispersion. Xiong *et al.* [9,10] also found that Mn-Fe spinels rarely produced N_2O side reactions in the presence of water. Liu *et al.* [11] prepared $FeVO_4/TiO_2$ catalysts that exhibited high activity in the medium temperature range, which is attributed to the enrichment of VO_x active species on the surface of $FeVO_4$ phase, thus accounting for the high N_2 selectivity and H_2O/SO_2 durability. Ma *et al.* [12] prepared $Fe_2(SO_4)_3/TiO_2$ catalysts by impregnation using $Fe_2(SO_4)_3$ as the precursor, which also showed excellent SCR performance in the medium to high temperature range, with NO_x conversion kept above 98 % between 350 °C and 450 °C.

Although iron-based metal oxide catalysts offer numerous advantages that ensure their excellent SCR performance, plenty of issues including insufficient low-temperature activity and severe catalyst deactivation caused by H_2O, SO_2, alkaline metals, and heavy metals limit their further application in certain practical scenarios. Therefore, excellent low-temperature activity, wide temperature window, high operating stability, strong H_2O/SO_2 durability and significant resistance to alkaline/ heavy metal poisoning are the key challenges currently remained for the development and application of highly efficient iron-based metal oxide catalysts. This review provides a comprehensive summary of the chemical properties, reaction mechanisms and promotional strategies on both catalytic activity and anti-poisoning performance associated with various types of iron-based catalysts, such as Fe_2O_3-based oxide catalysts, iron-based composite oxide catalysts, iron-based acidic salt catalysts and iron-based supported catalysts. And the SCR performance of different iron-based metal oxide catalysts with different modification strategies is further aggregated and summarized in Table S1 (Supporting information). The aim of this review is to offer a comprehensive understanding of iron-based metal oxide catalysts and to provide scientific insights and design strategies for the development and application of novel iron-based catalysts with improved catalytic activity and anti-poisoning ability for NO_x reduction (Fig. 1).

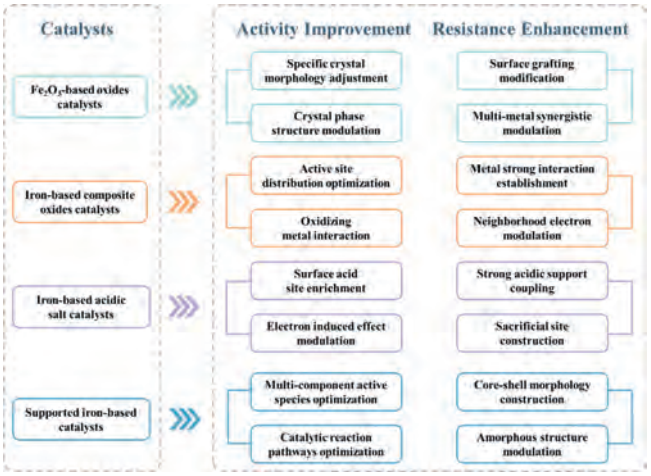


Fig. 1. Promotional strategies of catalytic activity improvement and anti-poisoning performance enhancement over iron-based metal oxide catalysts for NO_x reduction.

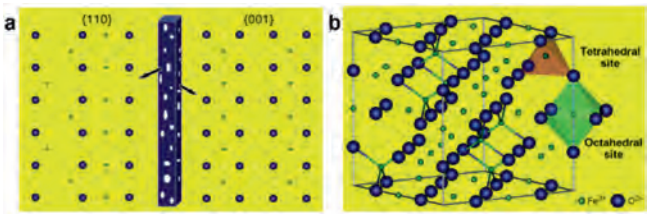


Fig. 2. (a) The real shape of γ-Fe_2O_3 nanorods and surface atomic configurations of the preferentially exposed and planes. (b) Atomic illustration of a cubic symmetry and the coordination patterns of tetrahedral and octahedral Fe^{3+} and O^{2-} species. Reproduced with permission [5]. Copyright 2012, Wiley.

2. Fe_2O_3-based oxides catalysts

For Fe_2O_3-based catalysts, the issue of narrow operational temperature window persists, particularly with poor activity at low temperatures and suboptimal N_2 selectivity at high temperatures. In response to these issues, most research has focused on modifying the crystalline phase and surface structure of Fe_2O_3-based oxide catalysts, as well as improving their surface acidity and redox properties, in order to improve their catalytic activity, N_2 selectivity, thermal stability and resistance to H_2O/SO_2 poisoning.

2.1. The effects of crystal structure and morphology

The crystal phase and morphology exhibit a significant effect on the NH_3-SCR performance of Fe_2O_3-based catalysts. The surface structure and morphology of Fe_2O_3 can be controlled by adjusting the crystal phase structure and specific crystal faces. By modifying the exposed high activity crystal faces, the density of surface active sites and intrinsic activity can be significantly increased to achieve optimal catalytic performance. In more details, two types of Fe_2O_3 with different crystal structures are commonly used in catalytic reactions, namely hematite (α-Fe_2O_3) and magnetite (γ-Fe_2O_3), among which the magnetite γ-Fe_2O_3 with slightly weaker thermal stability would tend to transform into hematite α-Fe_2O_3 at higher temperature [13,14]. Mou *et al.* [15] creatively prepared α-Fe_2O_3 and γ-Fe_2O_3 nanorod catalysts by liquid precipitation method and calcination/reflux method, respectively. The hematite and magnetite materials possessed the same nanorod morphology but completely different exposed crystal facets. When the γ-Fe_2O_3 nanorods was preferentially exposed the active crystal planes of (110) and (100), more active Fe^{3+} and O^{2-} sites were maintained simultaneously, which synergistically promoted the adsorption and activation of NO and NH_3, thus achieving better NH_3-SCR activity of 80 % NO conversion and 98 % N_2 selectivity in the range of 200-400 °C (Fig. 2) [5].

In addition to Fe_2O_3 nanorod catalysts, Wang *et al.* [16] discovered that the as-prepared Fe_2O_3 nanoparticles also showed high activity in the NH_3-SCR reaction over a wide temperature range of 150-270 °C. Liu *et al.* [17] prepared nanoporous α-Fe_2O_3 with different specific surface areas *via* heat-treating α-FeOOH. It is interesting to find that higher heat treatment temperature increased the crystallinity of α-Fe_2O_3, thus reducing surface oxygen defects and impairing catalytic activity. Gong *et al.* [18] used MIL-100 (Fe) as precursor and template to prepare a novel porous α-Fe_2O_3 nanostructured catalyst with retained morphological structure through a two-step controlled calcination process, which is responsible for high BET surface area and surface oxygen content, as well as improved reducible and acid properties. Teng *et al.* [19] also

used a hydrothermal method to control the exposed crystal faces of Fe_2O_3, namely (012), (014), and (113), and then loaded Fe_2O_3 onto TiO_2. The Fe_2O_3/TiO_2 catalyst with the (113) exposed surface exhibited the highest activity, which is attributed to its enhanced redox ability, increased surface active oxygen and acid sites, and a modified reaction pathway. Wang *et al.* [20] further demonstrated the influence of morphology and crystal facets of α-Fe_2O_3 on the activity using a combination of experimental methods and density functional theory (DFT). The researchers prepared three forms of α-Fe_2O_3: α-Fe_2O_3-S (rod-like; mainly exposed (110) and (012) facets), α-Fe_2O_3-R (rod-like; mainly exposed (110), (104) and (012) facets), and α-Fe_2O_3-C (cubic; only exposed (104) facet). DFT calculations indicated that NO and NH_3 adsorb more readily on the (110) and (012) facets, while O_2 dissociated more readily on the (110) facet. Furthermore, the (110) facet showed the lowest energy barrier for the decomposition of intermediate NH_2NO, thus enhancing the catalytic activity of α-Fe_2O_3-S. In addition, due to the exposure of highly active crystalline surfaces, α-Fe_2O_3-S still exhibited excellent stability in cycling tests at 330 °C and the catalytic performance was largely unaffected by the introduction of 5 % H_2O and 100 ppm SO_2. Gao *et al.* [21] used DFT calculations and experimental measurements to elucidate the NH_3-SCR reaction path on α-Fe_2O_3 (012) surface at the atomic level. Unlike the common insight of NH_3 activation acting as the rate determine step in SCR catalytic systems, the reaction tended to depend more on the NO activation process. In more details, NO was activated at Fe sites and then reacted with NH_3 to generate NH_2NO intermediates, which is further decomposed into N_2 and H_2O. Subsequently, the Fe sites on the catalyst with lower valence state was regenerated by O_2 assisted surface dehydrogenation. Thus, the NO activation and NH_2NO formation turned to be the rate determined steps of the entire SCR reaction (Fig. S1 in Supporting information). This study indicated that the introduction of promoters could help to facilitate the activation of NO so that the barrier of the rate-determining step was reduced and the low-temperature SCR activity of α-Fe_2O_3-based catalysts was effectively promoted.

In the case of α-Fe_2O_3, adsorbed NH_3 can react with gaseous NO, and gaseous NO is more readily adsorbed on α-Fe_2O_3 than gaseous NH_3, resulting in the formation of a stable nitrate that blocks the active sites, which subsequently leads to a decrease in catalytic activity. Compared to α-Fe_2O_3, γ-Fe_2O_3 shows a better catalytic activity in the range of 150-300 °C, because NH_3 and NO_x are more easily adsorbed and reacted with each other on the surface of γ-Fe_2O_3 [22]. In order to study the reactive iron sites in the γ-Fe_2O_3 based catalysts, Qu *et al.* [23] replaced the octahedral Fe^{3+} or tetrahedral Fe^{3+} sites with inactive Ti^{4+} or Zn^{2+}, and found that the catalytic activity of catalysts after doping Ti^{4+} was unchanged while that after doping Zn^{2+} was decreased, indicating that the tetrahedral Fe^{3+} sites were the real active sites among the SCR reaction. Therefore, how to increase the Fe^{3+} content in tetrahedra is quite necessary to the promotion of catalytic activity for γ-Fe_2O_3 based catalysts.

2.2. Promotional strategies of Fe_2O_3-based catalysts

2.2.1. Crystal phase structure modulation

In terms of the relatively active γ-Fe_2O_3 catalysts, improving the thermal stability and inhibiting the catalytic oxidation of NH_3 to NO at high temperature are beneficial to widen the temperature window. Therefore, it is quite necessary to modulate the crystal phase structure of Fe_2O_3-based catalysts to exhibiting enhanced catalytic performance. An effective way to inhibit the conversion of γ-Fe_2O_3 to α-Fe_2O_3 is to replace some Fe^{3+} species with other kinds of metal cations, such as Nb, Mo or La [24]. It was found that the strong interaction between Fe and Nb promotes γ-Fe_2O_3 formation in the presence of CTAB at suitable Fe/Nb [25]. And at high doping levels, Nb significantly increased the thermal stability of γ-Fe_2O_3 by occupying vacancies in the γ-Fe_2O_3 lattice and expelling a small amount of Fe^{3+} to compensate for the Nb^{5+} charge [26]. Moreover, La doping could effectively increase the activation energy of the phase transition of γ-Fe_2O_3, significantly raising its phase transition temperature from 350 °C to 650 °C [27]. In addition, the incorporation of manganese oxides has been shown to be an effective method of maintaining the γ-Fe_2O_3 phase at high temperatures [28]. Researchers have shown that different preparation methods can significantly improve the low-temperature activity and selectivity of Mn-modified γ-Fe_2O_3 [29]. Moreover, several studies have shown that grafting with heteropoly acid (HPA) can also inhibit the recrystallisation and phase transition from γ-Fe_2O_3 to α-Fe_2O_3. Geng *et al.* [30] grafted tungstophosphoric acid (HPW) onto γ-Fe_2O_3, resulting in higher catalytic activity within the wide temperature range of 250-500 °C. Iron oxides primarily existed as Fe_3O_4 in the HPW/Fe_2O_3 catalyst, which reduced the structural strain that led to phase transitions (Fig. 3). In addition, grafting with HPW provided higher acid strength, which increased the NH_3 adsorption capacity, thereby ensuring improved catalytic activity, N_2 selectivity and widened the operating temperature window.

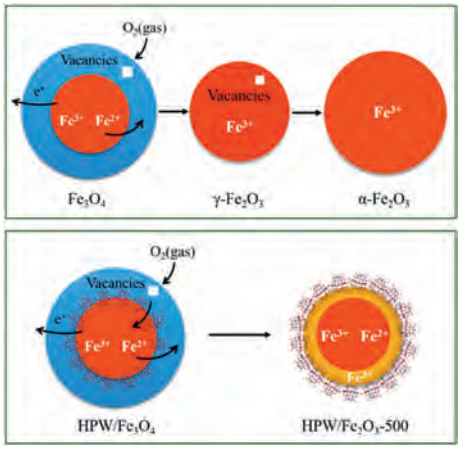


Fig. 3. Scheme of the phase transition inhibition of γ-Fe_2O_3 to α-Fe_2O_3 at 500 °C by HPW grafting. Reproduced with permission [30]. Copyright 2018, American Chemical Society.

2.2.2. Specific crystal morphology adjustment

In addition, researchers also have made many attempts to structurally design and modify iron oxide catalysts with specific morphologies to improve NH_3-SCR activity, SO_2 resistance and N_2 selectivity as well. Ren *et al.* [31] prepared Fe_2O_3 nanoring decorated by 12-tungstophosphoric acid (TPA), which exhibited high NH_3-SCR activity and SO_2 resistance due to the interaction between the Fe^{3+} of Fe_2O_3 nanoring and terminal oxygen of TPA. The HPW-modified circular Fe_2O_3 catalysts also enabled excellent NH_3-SCR activity and SO_2 resistance due to the synergistic effect of HPW polyoxoanion with Fe species on the external and internal surfaces of the nanosphere [32]. Except for the specific morphology modification, it was reported that Mn_2O_3-doped Fe_2O_3 hexagonal microchips maintained 98 % NO_x conversion at 200 °C for 60 h continuously. This demonstrated that Mn_2O_3 doping not only broadened the operating temperature window of the catalyst, but also exhibited excellent thermal stability. Among them, Mn_2O_3 nanocrystals played a key role in the low-temperature activity, mainly including greatly increased lattice oxygen, chemisorbed oxygen and adsorbed ammonia species [33]. Beyond that, it was reported that a novel type of core-shell catalysts with a hexagonal Fe_2O_3 core and a thin $Fe_2(SO_4)_3$ shell promoted the reactivity due to the activation of reactants at the interface of Fe_2O_3 and $Fe_2(SO_4)_3$ [34]. And ow-

ing to the unique hexagonal morphology structure and the protection of $Fe_2(SO_4)_3$ shell layer, the catalyst could still maintain high catalytic activity and operational stability when 300 ppm SO_2 and 10 vol% H_2O were introduced. The following studies on the properties of surface active species and reaction mechanism of the sulfuric acid-modified nano-plate Fe_2O_3 catalysts by time-resolved DRIFTS showed that the N_2 selectivity of modified catalysts was greatly improved and the surface NH_4^+ and NO_2^- species involved in the catalytic cycle were effective in the conversion of $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$ (Fig. S2 in Supporting information) [35].

In summary, several effective modification strategies including crystal phase structure modulation, adjustment of crystal morphology, surface grafting modification and multi-metal synergistic modulation have been reported for the modification of Fe_2O_3-based catalysts. These modifications not only significantly enhance NH_3-SCR activity and N_2 selectivity, but also improve thermal stability and resistance to SO_2/H_2O. As a result, all these effective promotional strategies greatly expand the applicability of iron oxide catalysts and lay a solid foundation for future research in the field heterogeneous catalysis.

3. Iron-based composite oxides catalysts

3.1. Research progress of iron-based composite oxides

In addition to the subtle design of Fe_2O_3 catalytic components and elaborate corresponding investigation of catalytic performance, numerous iron-based oxide catalysts and iron-containing composite oxides have been extensively considered to further improve the NO_x reduction catalytic activity and anti-poisoning performance as well. FeO_x can always positively enhance the catalytic activity of iron-based composite oxide catalysts, particularly improving catalytic activity within the medium to high temperature range and resistance to sulfur dioxide poisoning whether utilized as the active components or additives in iron-based composite oxide catalysts. Consequently, researchers have consistently incorporated other kinds of metal or non-metal components into iron oxides or doped Fe species into other metal oxides to enhance the redox properties and acidity of the NO_x reduction catalysts. All these strategies aim to improve the low-temperature SCR performance, expand the operating temperature window, as well as enhance the N_2 selectivity and resistance to SO_2 poisoning.

3.1.1. Iron oxides as active species

When Fe serves as the active site, metal oxides such as WO_3, CuO, and MnO_2 can be introduced to modulate the balance between acidity and redox properties in iron-based metal oxide catalysts [36–38]. Ma *et al.* [39] revealed the effects of Cu and W oxides modification on the redox properties and acidity of iron oxide catalysts and established the relationship between species composition, acidity and redox behavior of iron oxide catalysts. The results showed that appropriate doping of W and Cu oxides significantly increased the specific surface area of the catalyst, improving both Brønsted and Lewis acidities, and adjusting the surface species composition. This effective modification successfully facilitated the catalyst in achieving a high NO_x conversion of 90 %, a wide operational temperature window of 235-520 °C, high N_2 selectivity, and excellent resistance to water and sulfur dioxide. Similarly, Wang *et al.* [40] used a simple solvent-free method to synthesize WO_3-FeO_x catalysts with varying WO_3 contents and found that the optimal catalytic performance was achieved when the WO_3 content reached 30 %. This is mainly attributed to the NH_3-SCR reaction occurring *via* both the Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) pathways, where adsorbed NO rapidly reacted with adsorbed NH_3 and NH_4^+ to form N_2 and H_2O (Fig. 4).

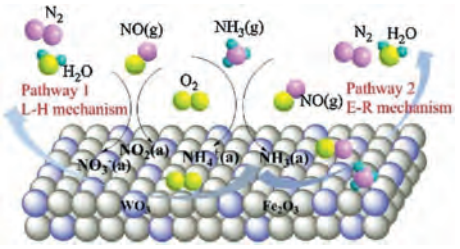


Fig. 4. The possible NH_3-SCR reaction mechanism over the WO_3-FeO_x catalyst for NO_x reduction. Reproduced with permission [40]. Copyright 2020, Elsevier.

In addition, appropriate acidification effectively inhibited the overoxidation of NH_3, thereby increasing the N_2 selectivity. It is found that Fe_2O_3 supported on hexagonal WO_3 nanorods also exhibited excellent SCR performance [41]. This can be attributed to the synergistic effect between the abundant acidic sites provided by WO_3 and the redox sites provided by Fe_2O_3, which not only effectively enhanced the low-temperature activity of the catalyst, but also imparted ideal tolerance to K, SO_2, and H_2O. Moreover, Fe-Ti spinel oxides exerted enhanced SCR performance as well, which is mainly resulted from the promoted acidity due to Ti incorporation. In the sight of catalytic reaction pathways, when Ti was incorporated into Fe_2O_3, the L-H pathway was suppressed while the E-R pathway was promoted. Beyond that, the improved catalytic activity was also greatly related to the oxidation ability of Fe^{3+} on the catalyst surface, the adsorbed NH_3 concentration, and the reducible Fe^{3+} concentration [42]. When V and Mn species were added to Fe-Ti spinel, the NO_x conversion increased significantly, especially within the range of 200-300 °C. The promotional effects of adding V species to Fe-Ti spinel on the SCR reaction was more obvious than that of Mn species, so that the Fe-Ti-V spinel exhibited much higher SCR activity, N_2 selectivity and H_2O/SO_2 durability within 250-400 °C.

In summary, when iron oxide is used as the active components for SCR catalysts, the incorporation of Cu, W, Mn, Ti or V oxide species into the catalysts can significantly modulate the concentration of Fe^{3+} species as well as the acidity, thermal stability and redox properties. The addition of these modified metal oxides can effectively enhance the SCR activity of iron oxide catalysts at low temperatures and also reduce the selectivity for N_2O formation. This allows the modified catalysts to exhibit effectively improved SCR activity, N_2 selectivity, and H_2O/SO_2 durability within a certain temperature range.

3.1.2. Iron oxides as additive species

Apart from acting as active components, numerous studies have investigated the promotional effects of iron species doping on the N_2 selectivity and resistance to SO_2 poisoning in other metal oxide catalysts, such as manganese oxides and cerium oxides. As an additive in NH_3-SCR catalysts, FeO_x can significantly increase the catalytic activity of metal oxide catalysts and improve their resistance to sulfur dioxide poisoning. Compared to MnO_x and FeO_x catalysts, FeMn composite oxides were more effective in improving the NH_3-SCR performance [43,44]. Fe species doping obviously increased the specific surface area of catalysts, thereby providing more acid sites and active sites. Meanwhile, Fe doping also led to more defects, including charge imbalance, unsaturated chemical bonds and oxygen vacancies. Moreover, the introduction of iron species significantly increased the concentration of Mn^{4+} and adsorbed oxygen on the surface, increased the ability of adsorbing and activation to NO, thus improving catalytic performance. The Fe-doped Mn-Eu catalysts also exhibited excellent low-temperature SCR activity and H_2O resistance due to the strong interaction among Mn, Eu and Fe components. The NO_x conversion reached 98 % at 100 °C and re-

mained around 90 % at 230 °C even under the condition of high gas hourly space velocity (GHSV) of 75,000 h^{-1} and the presence of 15 % H_2O for 50 h [45].

Additionally, it should be noted that different amounts of iron species additives give rise to two types of compensation mechanisms: vacancy compensation and dopant interstitial compensation. These compensation mechanisms can affect the structure and chemical properties of various SCR catalysts, including electronic state, reductive properties and surface acidity, thereby affecting catalytic performance. Hu *et al*. [46] synthesized a series of MnO_x-$Mo_y/Ce_{0.75}Zr_{0.25}O_2$ (M = Fe, Co, Ni, Cu) catalysts *via* an impregnation method and found that the MnO_x-$FeO_y/Ce_{0.75}Zr_{0.25}O_2$ catalyst exhibited improved low temperature activity and a wider temperature window. In addition, the iron oxide was well dispersed on the catalyst surface, preventing agglomeration of active species and promoting strong interactions between the active species and supports. More importantly, *in situ* DRIFTs experiments confirmed that bidentate nitrates were the common active species on these catalysts and that the reactivity of gaseous NO_2 and bridged nitrates increased with the addition of Fe species (Fig. S3 in Supporting information).

Doping of iron oxide species to form composite metal oxides can improve the structure and chemical properties of catalysts by affecting the crystallinity of metal oxides, the dispersion of surface active species, and the pore structure as well as pore size distribution. More importantly, the interaction between the doped iron species and initial metal oxide species also influenced the Fe^{3+} content, surface adsorbed oxygen, as well as the redox properties and acidity, ultimately improving the catalytic performance of the metal oxide composites SCR catalysts. However, for most of the iron-based metal oxide composite catalysts discussed above, the operating temperature window remains suboptimal. Therefore, further improvements in the redox properties related to low-temperature activity and the acidity properties associated with high-temperature activity are essential for enhancing the SCR performance of iron-based composite catalysts.

3.2. Promotion strategies of iron-based composite oxides

3.2.1. Active species distribution optimization

Different preparation methods can influence the specific surface area, microstructure, dispersion of active components, valence state distribution of elements, redox properties and surface acid sites of the iron-based composite oxides catalysts. Therefore, the performance of iron-based composite oxides SCR catalysts can be further improved by adjusting the synthesis conditions to optimize the distribution of active species on the catalyst surface without changing the composition of catalysts.

Xiong *et al*. [47] found that the iron-cerium composite oxide catalysts synthesized by micro-emulsion method owned excellent catalytic NO_x reduction performance as a result of moderate oxidizing ability, large specific surface area and rich acidic centers. Whereas, the corresponding catalysts prepared by the sol-gel method expressed better SCR activity but poor N_2 selectivity. Wang *et al*. [48] obtained NiFe composite oxides by calcining a hydrotalcite-like precursor and found that its catalytic performance was highly correlated with the phase composition that susceptible to the calcination temperature. The MO_x phase (M = Ni or Fe) formed at a lower calcination temperature would raise the content of Fe^{2+} and Ni^{3+}, which helped to improve the redox properties and low-temperature activity. The $NiFe_2O_4$ phase that formed at a higher calcination temperature made more Fe species appeared on the catalyst surface and formed a more stable structure (Fig. 5). Given all that, better SCR activity at high temperatures, resistance to SO_2 and operating stability were achieved simultaneously. Chen *et al*. [49] calcined the MnFeAl-NO_x layered double hydroxide

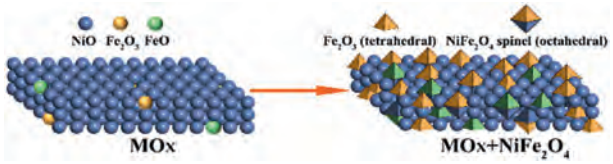


Fig. 5. The ideal model of catalysts with MO_x (M = Ni or Fe) or multiple phases (MO_x and a $NiFe_2O_4$ spinel) for NO_x reduction. Reproduced with permission [48]. Copyright 2018, MDPI.

(LDH) precursor to synthesize $MnFeAlO_x$, which presented a higher catalytic performance than the traditional doped Mn-Fe/γ-Al_2O_3 catalysts in a widely low temperature range (80-250 °C). The addition of iron species greatly increased the acidity, mobility of oxygen and amount of oxygen adsorbed on the catalyst surface. At the same time, it also significantly reduced the formation rate of SO_4^{2-} thereby suppressing the sulfur dioxide poisoning of the $MnFeAlO_x$ catalysts. This allowed the catalyst not only own a wide temperature operating window, but also to maintain excellent operating stability at 150 °C after the introduction of 100 ppm SO_2.

In summary, the optimization of active species distribution can be achieved by adjusting the synthesis methods and conditions of iron-based composites oxide catalysts, such as precursors and calcination temperature adjustment, which can help to improve the redox properties and low-temperature catalytic activity of catalysts. In addition, the interaction effects of active Fe species with other modified metals is confirmed to be another important factor to influence the NO_x reduction catalytic performance.

3.2.2. Active metals strong interaction establishment

Apart from the above discussion about adjusting synthesis methods to optimize the catalytic performance of iron-based composite oxides SCR catalysts, researchers also applied other kinds of active metal elements to the iron oxides or iron-based binary composite oxides to form a ternary or even quaternary mixed oxide catalytic system, aiming at establishing active metals strong interaction and further improving the catalytic activity by appropriate modulation of the preparation methods. For example, the introduction of additional metal oxides to Fe_2O_3/TiO_2 catalysts had been shown to further enhance the low-temperature SCR activity and resistance to SO_2 poisoning. Zhan *et al*. [50] prepared the Ce-doped FeTi catalysts by sol-gel method, whose NO_x conversion efficiency could achieve more than 95 % at 200 °C. The strong interaction between CeO_x, FeO_x and TiO_2 resulted in a larger amount of Ce^{3+}, more active chemisorbed oxygen and Brønsted acid sites so that the catalyst expressed excellent low-temperature SCR activity. In addition, WO_x-modified Fe_2O_3/TiO_2 catalysts owned increased abundance of surface acid sites and reactive oxygen sites greatly enhanced the resistance to H_2O and SO_2. However, Zhao *et al*. [51] further found that hydrothermal aging decreased the specific surface area of the catalysts, causing agglomeration or crystallization of Fe and W species, which led to a decrease in the acid content and surface-adsorbed oxygen content of the catalysts, resulting in a decrease in low-temperature activity. The Fe-Ti-Nb catalysts with suitable acidity and reducibility yielded a higher than 90 % NO_x conversion efficiency within the range of 200-400 °C. The addition of Nb species efficiently increased the acidity of Fe-O-Ti centers and certainly reduced the strong reducibility. Besides, the formation of a large amount of Lewis acids and Brønsted acids on the catalyst surface as well as the formation of active *cis*-$N_2O_2^{2-}$ and monodentate nitrate species both promoted the improvement of the SCR reaction activity (Fig. S4 in Supporting information) [52]. The addition of Nb species would cause a double redox reaction ($Ce^{4+} + Nb^{4+} \leftrightarrow Ce^{3+} + Nb^{5+}$ and $Fe^{2+} + Nb^{5+} \leftrightarrow Ni^{3+} + Nb^{4+}$) to generate more oxygen vacancies and unsaturated chemical bonds

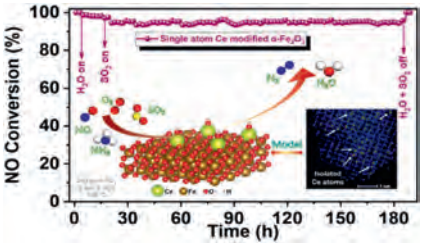


Fig. 6. The possible NH_3-SCR reaction mechanism over single-atom Ce-modified α-Fe_2O_3 catalysts for NO_x reduction. Reproduced with permission [55]. Copyright 2022, American Chemical Society.

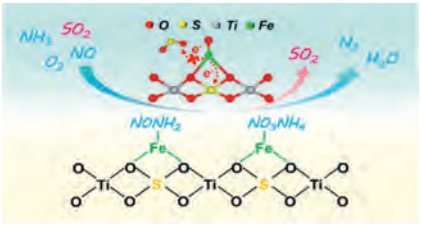


Fig. 7. The proposed NH_3-SCR reaction mechanism and resistance to SO_2 poisoning over the Fe_2O_3/S-TiO_2 catalyst for NO_x reduction. Reproduced with permission [57]. Copyright 2022, American Chemical Society.

on the catalyst surface, which increased the redox performance in turn.

Although extensive research has been conducted on the modification of iron-based oxides catalysts, their low-temperature activity still has significant room for improvement. Therefore, the combination of iron-based catalysts with strongly oxidative metal oxides is essential to further broaden the active low-temperature window range. Fang *et al.* [53] reported that the $Fe_{0.3}Mn_{0.5}Zr_{0.2}$ catalyst exhibited significantly enhanced low-temperature catalytic activity and an extended operating temperature window due to the synergistic interactions among Zr, Fe, and Mn species. In addition, it maintained excellent thermal stability and SO_2 resistance at 200 °C, even in the presence of 200 ppm SO_2. When Fe_2O_3 was loaded on $ZrTiO_4$ supports with a porous structure, strong Fe-Zr-Ti interactions were also achieved. The highly dispersed active sites and abundant Lewis acid sites on the catalyst surface not only improved the low-temperature SCR performance, but also enhanced the resistance to SO_2 poisoning [54]. Chen *et al.* synthesized single-atom Ce-modified α-Fe_2O_3 catalysts by a citric acid-assisted sol-gel method. The highly dispersed Ce atomic cores maximized the formation of Ce-O-Fe bonds, which facilitated the reaction between adsorbed intermediates and gas-phase reactants. In addition, in the presence of SO_2, sulfate species deposited on the catalyst surface can decompose at relatively low temperatures, thus demonstrating excellent sulfur dioxide tolerance (Fig. 6) [55]. It can be concluded that the introduction of various metal oxides increases the resistance of iron-based catalysts to H_2O and SO_2 through two primary mechanisms: First, metal oxides can act as sacrificial sites that preferentially adsorb SO_2, thereby preventing sulfation of active FeO_x species. Second, metal oxides can decline the decomposition temperature of $(NH_4)_2SO_4$, facilitating a balance between the formation and decomposition of poisoning species, thereby exposing more active sites for catalytic reactions.

In addition, plenty of studies on the modification of iron-based catalysts by the introduction of non-metallic elements have also been widely reported. Song *et al.* [56] prepared $Fe_aS_bTiO_x$ catalysts whose operating temperature window in NH_3-SCR reaction was significantly expanded due to the synergistic effect between Fe and sulfur species. This is because sulfur existed as a kind of stable SO_4^{2-} species, which greatly increased the stability and amount of Brønsted and Lewis acid sites and enhanced the adsorption of NH_3, thus significantly inhibiting the excessive oxidation of NH_3 caused by pure iron species. Moreover, with the introduction of SO_4^{2-}, the electronic interaction between SO_4^{2-} and TiO_2 support was modulated, the Lewis acidity was enhanced, and the Fe species were more charge-deficient. The charge transfer process between Fe_2O_3 and SO_2 was weakened while boosted that between NO/NH_3 and Fe_2O_3 by SO_4^{2-} doping, thus Fe_2O_3/S-TiO_2 revealed excellent NO_x reduction performance and SO_2 tolerance (Fig. 7) [57]. Similarly, Fe-based catalysts modified with H_3PO_4 or H_2SO_4 showed significantly improved acid and NH_3 adsorption capacity, which not only resulted in high SCR activity, but also significantly improved resistance to alkali metal and heavy metal poisoning [58–60].

Consequently, the construction of effective multi-metal mixed oxides has been shown to significantly enhance the catalytic performance of iron-based composite catalysts. On the one hand, the strong interactions between various metal oxides significantly enhance the concentration of active oxygen and acid sites to achieve strong active metals interaction establishment; on the other hand, the dual redox cycle facilitates effective electron transfer between various catalytic components for neighboring electron modulation. In addition, certain non-metal oxides can promote catalytic cycling and alter gas adsorption behavior, thereby improving performance parameters such as low temperature SCR activity, N_2 selectivity and resistance to sulfur dioxide and water.

4. Iron-based acidic salt catalysts

4.1. Research progress of iron-based acidic salt catalysts

Typically, Fe-based acidic salts can usually be classified as Fe-based metal salts and Fe-based non-metal salts. Due to the strong electron transfer between Fe species and non-metallic acidic radicals (SO_4^{2-}, PO_4^{3-}) or metal acidic radicals (TiO_x^{3-}, VO_4^{3-}, WO_x^{3-}), the redox capacity and acidity of the Fe-based acidic salts catalysts are always greatly enhanced, resulting in excellent catalytic activity as well as tolerance to SO_2 and H_2O, which has led to the widespread design and application of iron-based acid salt catalysts for NO_x reduction reaction.

4.1.1. Iron-based metal acidic salt catalysts

In addition to the aforementioned iron-titanium spinel catalysts and Fe_2O_3/TiO_2 supported catalysts previously reported, iron titanate catalysts have received extensive attention due to their special microstructure and electronic properties. A series of iron titanate catalysts named as $Fe_aTi_bO_x$ with different molar ratios of Fe/Ti and a crystallite phase proposed by Liu *et al.* [61] showed excellent SCR activity, N_2 selectivity and operating stability within the medium temperature range. And the $FeTiO_x$ catalyst even showed more than 90 % NO_x conversion during 250-400 °C after the sulfation treatment for 48 h. Compared with TiO_2 and Fe_2O_3, the coexistence of Fe and Ti was beneficial to the formation of microcrystals with a specific Fe-O-Ti structure [62]. After a comprehensive study including the effects of different precursors and preparation methods on the structure and activity of iron titanate catalysts, it is found that iron titanate catalysts prepared with titanium sulfate as a precursor exhibited higher catalytic activity and N_2 selectivity than those prepared with titanium tetrachloride as a precursor and Fe_2O_3/TiO_2 supported catalysts. This is mainly due to the formation of iron-titanium crystals with a specific Fe-O-Ti structure [63]. Through in-depth exploration of the reaction mechanism at a relatively low temperature (<200 °C), the SCR process mainly followed L-H reaction mechanism. Among which NO was oxidized by oxygen to form the monodentate nitrate at the Fe^{3+}

site and this process was confirmed to be a rate-limiting step. At high temperatures (>200 °C), the SCR process mainly followed L-H reaction mechanism in which the formation of the intermediate species NH_2NO was the main speed-limiting step (Fig. S5 in Supporting information) [64]. The XAFS studied on the specific microstructure of active species and deoxidation behavior of $FeTiO_x$ catalysts manifested that the enhanced reducibility of Fe^{3+} species in $FeTiO_x$ crystallites was due to the electronic inductive effect of Fe and Ti species existing in the homogeneous edge shared Fe^{3+}-$(O)_2$-Ti^{4+} structure [65,66].

Tungsten is widely used as a catalyst stabilizer and promoter due to its high thermal stability and acidity, which contributes to an extended operating temperature range in the NH_3-SCR reaction and inhibits NH_3 oxidation. Researchers have gradually elucidated the role of iron tungstate in the catalytic process and the structure-activity relationship of iron tungstate catalysts. Liu *et al.* [7] reported that the introduction of WO_3 into Fe_2O_3 resulted in an increase in the content of Lewis acid sites, which inhibited the formation of inactive nitrates and made more active sites available for adsorption and activation of NH_3. Meanwhile, the synergistic effect between WO_3 and Fe_2O_3 enabled the WO_3/Fe_2O_3 catalyst to maintain moderate redox ability to effectively weaken the non-selective catalytic oxidation of NH_3, resulting in enhanced NH_3-SCR performance. Additionally, Zhang *et al.* [67] prepared $FeWO_x$ catalysts *via* different methods and found that N_2O was easily produced on the catalyst prepared by the impregnation method. While the catalyst prepared by the grinding method showed better catalytic activity owing to higher specific surface area, larger amount of Fe^{2+} and adsorbed oxygen species as well as more acidic sites. Meanwhile, the specific reaction pathways were differential as L-H mechanism dominating at low temperatures and E-R mechanism emerging at relatively high temperatures. Besides, in regard of the effects of calcination temperature, it was further confirmed that the optimal calcination condition was 500 °C, where surface defects and coexistence of $FeWO_4$ or WO_3 were present, resulting in the optimal NO_x reduction efficiency (Fig. S6 in Supporting information) [68].

Except for the discussion about iron titanates and iron tungstate catalysts mentioned above, related studies have found that utilizing the synergistic effects of iron and vanadium species can extend the operating temperature window and improve high-temperature N_2 selectivity in the NH_3-SCR reaction. Zhang *et al.* [69] found that adding certain amount of V species to form iron-vanadium mixed oxide catalysts could increase the activity and redox property of Fe_2O_3, which is resulted from the smaller grain size of Fe_2O_3 and higher redox ability. Moreover, Mu *et al.* [70] found that the vanadium-doped Fe_2O_3 catalysts presented excellent catalytic performance due to the improved redox ability and surface acidity. The NO_x conversion reached more than 90 % under a wide temperature window of 175-400 °C, with the N_2 selectivity and H_2O/SO_2 durability were also maintained at relatively high levels. Further characterization revealed that the incorporation of V species resulted in the formation of amorphous $FeVO_4$ and Fe_2O_3 with smaller particle size and higher oxygen mobility. The strong interaction between $FeVO_4$ and Fe_2O_3 species kept V in a higher valence state and the abundant VO_x species rather than FeO_x species on the catalyst surface acted as the main acid sites. The electron-inducing effects between Fe and V species promoted the charge transfer, which accelerated the oxidation of NO to NO_2, further improving the low-temperature catalytic performance and reducing the apparent activation energy (Fig. S7 in Supporting information).

4.1.2. Iron-based non-metal acidic salt catalysts

Sulfate containing catalytic materials have attracted much attention in the research of NH_3-SCR catalysts due to their high acidity and excellent resistance to SO_2 and H_2O. Ma *et al.* [12] synthesized the $Fe_2(SO_4)_3/TiO_2$ catalyst using $Fe_2(SO_4)_3$ as the precursor by the impregnation method and achieved a NO_x conversion of more than 98 % in the temperature range of 350-450 °C. Sulfate species played a crucial role in the SCR reaction, not only facilitating the generation and enhancement of Brønsted acid sites but also influencing the dispersion of active species on the catalyst surface. However, the thermal stability of the sulfate-containing materials was typically suboptimal. In more details, Yu *et al.* [71] investigated the effects of thermal stability on the SCR performance of $Fe_2(SO_4)_3/TiO_2$ catalysts and found that the decrease in catalytic activity after heat treatment was attributed to the decomposition of $Fe_2(SO_4)_3$ (the conversion of $Fe_2(SO_4)_3$ to α-Fe_2O_3), which reduced the Brønsted acid sites on the catalyst. However, the introduction of SO_2 into the gas stream resulted in the recovery of Brønsted acid sites, thus the NO_x reduction efficiency could return to the state before SO_2 inactivation (Fig. 8).

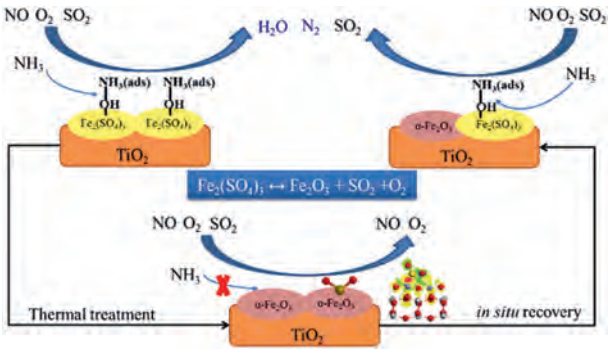


Fig. 8. The NH_3-SCR reaction mechanisms over the $Fe_2(SO_4)_3/TiO_2$ catalyst for NO_x reduction. Reproduced with permission [71]. Copyright 2019, Elsevier.

4.2. Promotion strategies of Iron-based acidic salt catalysts

4.2.1. Electron induced effect modulation

The NO_x reduction activity of iron-based acidic salt catalysts at low temperatures, especially for NO_x conversion below 200 °C, still needs to be further improved. It has been shown that the low-temperature SCR performance of $FeTiO_x$ catalysts can be further enhanced by introducing additional metal oxide species to promote the modulation of electron-induced interactions between various active metal species. Liu *et al.* [72] reported that partial substitution of Fe with Mn in iron titanate catalysts resulted in a significant enhancement in low-temperature activity, although a slight decrease in N_2 selectivity was observed. A high Mn content facilitated the oxidation of NO to NO_2 and increased the formation of monodentate nitrate species (MO-NO_2), which could readily react with NH_4^+ or NH_3 adsorbed on adjacent active sites to form more active intermediates that subsequently reacted with gaseous NO to produce N_2 and H_2O. In addition, it was observed that after partial substitution of Fe with Cr, the catalyst retained its crystallite structure and the SCR activity was significantly improved, especially at low temperatures [73]. The partial substitution of Cr effectively modified the surface properties, porosity and the ratio of Lewis acid sites to Brønsted acid sites in the catalyst, while also increased the mobility of lattice oxygen and improved the oxidation capability of the modified catalyst. Similarly, CeO_2 doping can effectively improve the low temperature performance of $FeTiO_x$ catalysts, which was due to the formation of Fe-O-Ce structures significantly improved the redox capability of the catalyst, facilitating the oxidation of NO and activation of NH_3 at low temperatures [74].

Moreover, we found that the $Fe_\delta Ce_{1-\delta}VO_4$ catalyst not only exhibited a strong inhibition capacity on SO_2 adsorption, but also effectively inhibited the deposition of sulfate species, which en-

dowed strong SO_2 resistance at the low temperature of 240 °C [75]. Meanwhile, the SCR activity of $Fe_\delta Ce_{1-\delta}VO_4$ was simultaneously improved by increasing the oxygen vacancy, enhancing the redox performance and improving acidity. Li *et al.* [76] proposed that phosphorus species exerted contrasting effects on NO_x reduction catalytic performance at low and high temperatures by examining the crystal structure, surface acidity, surface adsorbed species, and redox behavior of phosphorus-poisoned $FeTiO_x$ catalysts during the SCR reaction. Phosphorus species preferentially bonded with the electron-deficient Ti^{4+} and Fe^{3+} cations to form P-O-Fe and P-O-Ti bonds, thereby blocking the Lewis acid sites (Fe-NH_3 or Ti-NH_3), leading to a reduction in the acidity and a consequent loss of reactivity. However, the phosphate formed introduced additional Brønsted acid sites (P-O-NH_4^+) that facilitated the SCR reaction *via* L-H mechanism, providing a new reaction pathway that enabled the catalyst to exhibit improved reactivity and thermal stability at high temperatures (Fig. S8 in Supporting information).

The iron-tungsten composite oxide catalysts proposed by Wang *et al.* [77] exhibited high NO_x conversion and N_2 selectivity over a broad temperature range, while maintaining significant stability and relatively high NO_x conversion efficiency even in the presence of H_2O, SO_2, and CO_2. The synergistic effects of α-Fe_2O_3 and $FeWO_4$ species that formed after the introduction of W species greatly improved the surface acidity and electronic properties of the iron-tungsten catalyst. Additionally, $FeWO_4$ with an octahedral structure acted as Brønsted acid sites, facilitating the formation of highly active NH_4^+ species, thereby promoting the enhancement of SCR activity. By studying the effects of sulfurization on $FeWO_x$ catalysts, it was found that sulfurization inhibited the SCR activity at low temperatures (<300 °C) but had no significant effect at high temperatures (≥300 °C), which was caused that the formation of NO_2 was hindered after sulfurization, endowing the "Fast-SCR" reaction pathway to be partially interrupted and resulting in certain inactivation at low temperatures. However, at high temperatures, the formation of nitrate species altered the reaction pathways to L-H mechanism with NH_4NO_3 as an intermediate, so that the catalyst maintained relatively high anti-SO_2 poisoning performance (Fig. S9 in Supporting information) [78].

In summary, electron induced effect modulation can significantly enhance the redox capability of iron-based acidic salt catalysts, promoting the oxidation of NO to NO_2 at low temperatures, which effectively facilitates the "fast SCR" reaction process. Furthermore, coupling with acidic metal oxides or inorganic acids can greatly improve the surface acidity and promote the enrichment of surface acid sites, which positively accelerates the NH_3 adsorption and activation over iron-based acidic salt catalysts. Notably, the valid combinations of electron induced effect modulation and acidic additives coupling can significantly improve the low temperature catalytic activity as well as anti-poisoning ability against to SO_2 and alkaline metals of most iron-based acidic salt catalysts.

4.2.2. Strong acidic support coupling

In addition to increasing the acidity of iron-based acidic salt catalysts by acidic metal doping or inorganic acid modification, the coupling of strongly acidic supports not only increases the total acidity of catalysts, but also further help to disperse the active species. Among which $FeVO_4$ is usually supported on various supports such as TiO_2, Al_2O_3, and CeO_2, establishing strong interactions between the support and the active phase to further enhance the SCR performance. Liu *et al.* [11] synthesized a $FeVO_4/TiO_2$ catalyst that demonstrated excellent catalytic activity, high N_2 selectivity, and remarkable resistance to H_2O/SO_2 under medium-temperature conditions. The results revealed that the $FeVO_4$ active phase was highly dispersed on the support surface and abundant surface defects were present, which facilitated the adsorption and activation of reactants on the catalyst surface. Meanwhile, the interaction between Fe and V species partially inhibited the oxidation of NH_3 at elevated temperatures. Similarly, when $FeVO_4$ was supported on CeO_2, the high redox capability and acid content contributed to the enhanced SCR activity and SO_2 resistance of the catalyst [79]. Casanova *et al.* [80] controlled the homogeneity of stoichiometric Fe/V-rich compositions by adjusting the pH during the precipitation process of iron vanadate for the preparation of $FeVO_4$ supported on TiO_2-WO_3-SiO_2. This modulation in turn influenced the strong interaction between the vanadate components and TiO_2-WO_3-SiO_2, as well as the thermal stability of the catalyst. Homogeneous $FeVO_4$ which derived from stoichiometric $FeVO_4$ showed the optimal activity and thermal stability due to the acidity of V-O moiety and the characteristics of Fe^{3+}-O-V^{5+} bonds. The effect of phase composition on the TiO_2-WO_3-SiO_2 supported $Fe_xAl_{1-x}VO_4$ catalysts was further studied by varying the calcination temperature. The active species of the TiO_2-WO_3-SiO_2 supported $Fe_xAl_{1-x}VO_4$ catalyst in the NH_3-SCR reaction were verified to be VO_x species instead of $FeVO_4$. The well-dispersed VO_x species formed after decomposition owned a coordination environment similar to that of VO_x species on traditional vanadium-based catalysts. Meanwhile, VO_x species were finely dispersed on the surface of TiO_2-WO_3-SiO_2 support at high temperatures and then migrated to the WO_3 sites to maintain high SCR performance (Fig. S10 in Supporting information) [81].

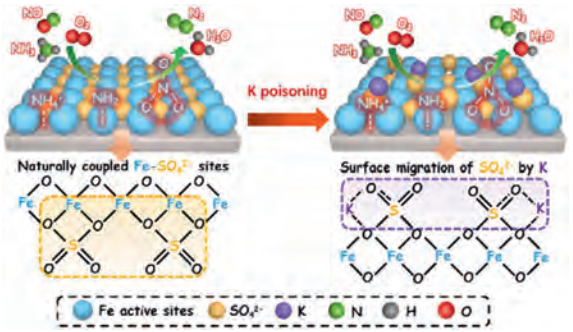


Fig. 9. Schematic illustration of the induced surface migration of SO_4^{2-} by K poisoning and the proposed K resistance mechanism over TiO_2-supported $Fe_2(SO_4)_3$ catalysts for NO_x reduction. Reproduced with permission [82]. Copyright 2021, American Chemical Society.

Similarly, Feng *et al.* [82] demonstrated that TiO_2-supported $Fe_2(SO_4)_3$ catalysts exhibited both high NO_x reduction efficiency and alkali metal resistance over a fairly wide temperature window of 200-500 °C. Sulfate species which tended to migrate from the bulk phase to the surface remained largely on the catalyst, effectively binding to the alkali metal K cations to release poisoning effects on the active iron sites. The adsorption capacity and rate of NH_3 and NO remained steady due to the protective effects of migrating sulfate and the close coupling with the Fe active sites, so that the tightly coupled Fe metal sites and sulfate species played important roles as highly active sites and unique poisoning sites on the self-preserving TiO_2-supported $Fe_2(SO_4)_3$ catalysts (Fig. 9). Li *et al.* [83] further found that phosphate modification of Fe_2O_3/TiO_2 catalysts significantly enhanced the resistance to alkali metal poisoning during the reduction of NO_x. The introduction of phosphates led to the formation of iron phosphate species, whose tetrahedral structure provided additional Brønsted acid sites, increasing the surface acidity of the catalyst. At the same time, the formation of Fe-O-P bonds enhanced the redox capability and increased the surface adsorption of oxygen on the catalyst. Moreover, potassium preferentially interacted with the phosphate group (PO_4^{3-}), which helped preserve the iron species at the active sites.

In conclusion, coupling with strong acidic supports over iron-based acidic salt catalysts can effectively modulate the interaction effects between the supports and active sites to further disperse the active iron sites and promote the adsorption activation of NH_3 as well. In addition, iron-based acidic salt catalysts modified with sulfuric acid or phosphoric acid readily realize the construction of sacrificial sites that preferentially bind to the alkali metal poisons, thus releasing the active iron sites to maintain excellent redox property and reactants adsorption capacities as well, which endows the catalyst to exhibit high deNO_x activity even after alkali metal poisoning. However, the thermal stability of sulfate-containing iron-based acidic salt catalysts is generally suboptimal, which should be pay more attention to further improve their thermal stability while ensuring high SCR activity, N_2 selectivity, and anti-alkali metal poisoning performance.

5. Supported iron-based catalysts

5.1. Research progress of supported iron-based catalysts

Generally, when the active components are supported on a suitable support, it is essential that the support provides a large specific surface area, which facilitates the dispersion of active components into smaller particles. In addition, some excellent chemical properties of the support itself can also improve the SCR activity and structural stability of catalysts under the reaction conditions. Common support materials used in supported iron-based catalysts include metal oxides (such as alumina, tungsten oxide, titanium dioxide), carbon materials (such as activated carbon, carbon nanotubes) and other clay materials (such as kaolin, diatomite.).

5.1.1. Metal oxides as supports

Metal oxide supports have been extensively studied due to the strong metal-support interaction and the electron transfer between active components. TiO_2 is commonly used as a support for denitration catalysts due to its high specific surface area, thermal stability, surface acidity and SO_2 resistance. The Fe/TNT (titania nanotube) synthesized by hydrothermal method and wet impregnation technique exhibited above 90 % NO_x conversion within the temperature window range from 200 °C to 350 °C due to the high dispersion of active species on the support [84]. Moreover, adjusting the crystal planes of supports or exploiting their morphological effects to modulate the interaction between Fe_2O_3 and supports is beneficial to improve the catalytic activity. Through the study of Fe_2O_3 catalysts supported on TiO_2 nanosheets (TiO_2-NS) and nanospindles (TiO_2-NP), Liu *et al.* [85] found that Fe_2O_3/TiO_2-NS exhibited better SCR activity at low temperatures, which is attributed to the presence of more acid sites, oxygen vacancies, and reactive oxygen species in the catalyst. The DFT results further indicated that the adsorption energy of NO and NH_3 on TiO_2-NS (001) was lower than that on TiO_2-NSP (101).

Besides, we also prepared CeO_2 nanorods (CeO_2-NR) and CeO_2 nanospindles (CeO_2-NSP) supported Fe_2O_3 catalysts, in which CeO_2-NR mainly exposed the (110) and (100) crystal planes and CeO_2-NSP mainly exposed the (111) crystal plane. It was found that Fe_2O_3/CeO_2-NR demonstrated higher NO_x reduction catalytic activity compared to Fe_2O_3/CeO_2-NSP. The DFT results revealed that NO and NH_3 presented higher reactivity on Fe_2O_3/CeO_2-NR than Fe_2O_3/CeO_2-NSP, which is caused that the (110) and (100) planes exposed on CeO_2-NR increased the surface adsorbed oxygen, oxygen vacancies and Fe atom density, resulting in high catalytic activity [86]. Moreover, Li *et al.* [41] supported Fe_2O_3 nanoparticles on hexagonal WO_3 nanorods, among where the crystal structure and morphology of Fe_2O_3 and WO_3 remained unchanged during the preparation of Fe_2O_3/WO_3. Due to the synergy between the redox sites provided by Fe_2O_3 and the acid sites provided by WO_3, the catalyst exhibited excellent low-temperature SCR activity and maintained high activity as well as operating stability in the presence of K, SO_2 and H_2O. To further investigate the reaction mechanism of Fe_2O_3/WO_3, Zhang *et al.* [87] anchored WO_3 on the surface of Fe_2O_3 nanosheets by impregnation to strength the submonolayer interactions between W and Fe, which further confirmed that the W-O-Fe interface was closely related to the active sites and played a crucial role in the SCR reaction process (Fig. S11 in Supporting information). Furthermore, when Fe_2O_3 was supported on MoO_3 nanobelts, it was observed that the layered structure of α-MoO_3 with different oxidation states and appropriate interlayer distances could trap NH_4^+ from NH_4HSO_4, thus promoting the decomposition of NH_4HSO_4 and enhance the SO_2 resistance [88]. When Fe_2O_3 was loaded on block or nanosheet MoO_3, Chen *et al.* [89] found that the supported iron-based catalysts showed superior low-temperature performance compared to Fe_2O_3 catalysts. In addition, the Fe_2O_3/MoO_3 nanosheets also exhibited higher SCR activity and N_2 selectivity, which could be attributed to their stronger NH_3 adsorption capacity and better redox properties. By analyzing the structural features and chemical properties of various metal oxides, we found that TiO_2 can help improve the dispersion of active Fe sites and SO_2 resistance due to its high specific surface area and excellent SO_2 tolerant ability, while CeO_2 can significantly improve the low-temperature catalytic activity of Fe-based catalysts due to its abundance of oxygen vacancies. WO_3 and MoO_2, as supports with abundant acid sites, can improve the SO_2 resistance of the catalysts by reducing the adsorption of SO_2.

In conclusion, when metal oxides are used as supports, the iron-based catalysts exhibit higher catalytic performance and SO_2 resistance. However, improving the stability of metal oxide supports and preventing the phase transition during the high-temperature reaction still remain as one of the urgent issues to be solved for supported iron-based catalysts. In addition, the acidity of some metal oxides is not that insufficient to provide enough acid sites to ensure smooth NH_3 adsorption and provide sacrificial sites for alkaline metal poisons. Therefore, it is also necessary to further develop effective solutions for improving the surface acidity of supported iron-based catalysts to enhance the NO_x reduction catalytic performance and anti-poisoning ability as well.

5.1.2. Carbon materials as supports

In recent years, carbon-based materials (such as activated carbon and activated coke) have attracted considerable attention due to their large specific surface area and well-developed pore structure, which can positively facilitate the homogeneous dispersion of active sites for iron-based NO_x reduction catalysts. Han *et al.* [90] anchored Fe_2O_3 nanoparticles onto carbon nanotubes (CNTs) by *in situ* ethanol-thermal method and found that the Fe_2O_3/CNTs catalyst exhibited a wider operating temperature window and higher SCR activity than those synthesized by impregnation and co-precipitation methods. This could be attributed to the high dispersion of Fe_2O_3 on the support surface, the enrichment of surface-active oxygen species, as well as stronger reducibility and acidity, which also endowed the catalyst with excellent operating stability, tolerance to H_2O and SO_2. Similarly, Yang *et al.* [91] found that when the calcination temperature of Fe_2O_3/activated carbon was increased from 400 °C to 500 °C, the conversion of α-Fe_2O_3 and γ-Fe_2O_3 was promoted and the dispersion of γ-Fe_2O_3 was improved, which resulted in the enhancement of SCR activity.

Due to the presence of numerous unsaturated bonds in the structure of activated carbon, oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups can always be formed readily *via* the reaction with certain oxidants, which significantly alters the chemical properties of activated carbon surface. Li *et al.* prepared $(NH_4)_2S_2O_8$ modified $Fe_2(SO_4)_3$/activated

carbon catalysts by oxygen functionalized pretreatment of activated carbon with $(NH_4)_2S_2O_8$, followed by impregnation with $Fe_2(SO_4)_3$. The catalyst achieved 100 % NO_x conversion at 170 °C and the NO_x conversion remained unchanged at 100 % after the introduction of 100 ppm SO_2 at 250 °C for 24 h. The results indicated that after modification with $(NH_4)_2S_2O_8$, the number of oxygen-containing functional groups on the catalyst surface increased, which enhanced the redox properties and facilitated the improvement of SCR performance. In addition, due to the interaction between the support and active component $Fe_2(SO_4)_3$, Fe^{2+} and SO_4^{2-} were adsorbed at different sites by electrostatic interaction, which promoted the decomposition of specific $Fe_2(SO_4)_3$ site to form the active $Fe_2(SO_4)_3$-Fe_2O_3 interface. The presence of Fe_2O_3 further improved the NO_x reduction efficiency, while the presence of $Fe_2(SO_4)_3$ imparted the catalyst with excellent sulfur resistance (Fig. S12 in Supporting information) [92,93].

Although carbon-based materials own a high specific surface area that contributes to the dispersion of active components, and the interaction between the support and active iron sites can be optimized by modulating the surface oxygen-containing functional groups to improve the catalytic activity at low temperatures, there is still consider room for improvement. In addition, under high temperature and oxidative conditions, carbon-based materials can undergo oxidation or structural collapse, which present adverse effects on the NO_x reduction reaction. Therefore, how to further improve the low-temperature activity and thermal stability of carbon-based material-supported iron-based catalysts still needs to be studied in depth.

5.1.3. Other materials as supports

In addition, some environment friendly materials have recently been explored to act as support materials, such as attapulgite (ATP) [94], kaolin [95], molecular sieves [96], halloysite [97]. Due to the advantages of cheap and easy availability, sufficient acidity, large specific surface area and facile modification, the development of such support materials is of great importance for the industrialization of supported NH_3-SCR catalysts. Szymaszek *et al.* [98] conducted a comparative study of the utilization of natural layered clays (bentonite and vermiculite) and natural zeolite (clinoptilolite) as supports for NH_3-SCR catalysts. It was showed that iron-loaded catalysts (such as Fe-Clin and Fe-Bent) exhibited high SCR activity at medium and high temperatures (>250 °C), but their activity was limited at low temperatures. To address this issue, the use of mixed metal oxides, especially the commonly used Fe-Mn combination as active components, can greatly improve the low temperature catalytic activity due to the synergistic interaction between the various active species. Furthermore, Wang *et al.* [95] synthesized Fe-Mn catalysts supported on kaolin and diatomite, with the 12Fe10Mn/kaolin catalyst exhibited superior catalytic activity over the entire temperature range compared to the diatomite-supported catalyst due to improved dispersion of active species, enhanced low-temperature reduction performance, increased number of Brønsted acid sites, and higher ratio of Mn^{4+} to Fe^{3+}. Similarly, $MnFeTiO_x$ supported on attapulgite (ATP) and Fe-Mn/fly-ash-derived SBA-15 also exhibited excellent deNO_x activity during relatively low temperature (<300 °C) [96]. With the help of *in situ* DRIFT technology, Li *et al.* [96] thoroughly investigated the reaction mechanism of Fe-Mn/SBA-15 catalysts. Due to the strong reducing ability, high Mn^{4+}/Mn^{3+} atomic ratio and abundant adsorbed oxygen species, Fe-Mn/SBA-15 exhibited excellent low-temperature SCR performance. The results of *in situ* DRIFT indicated that the NH_3-SCR process on Fe-Mn/SBA-15 followed the Mars-van Krevelen, E-R and L-H mechanisms. However, due to the strong oxidation, low acidity and high basicity of the catalyst, a large amount of nitrate was formed and spontaneously decomposed to N_2O, leading to a decrease in N_2 selectivity (Fig. 10).

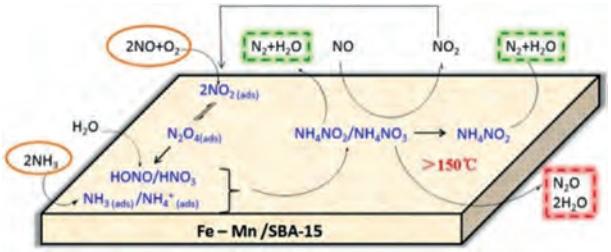


Fig. 10. The low temperature NH_3-SCR reaction mechanism over Fe-Mn/SBA-15 catalysts for NO_x reduction. Reproduced with permission [96]. Copyright 2018, American Chemical Society.

In conclusion, clay and zeolite materials contribute to the excellent catalytic performance of supported iron-based catalysts due to their abundant surface acid sites. However, their relatively weak redox properties limit the further improvement of low temperature NO_x reduction catalytic activity of the supported iron-based catalysts. Although coupling with metal oxides with strong oxidizing ability can improve the low-temperature catalytic activity to some extent, the improvement remains suboptimal. In addition, there is limited research on the inhibition of SO_2 and alkali metal poisoning and anti-poisoning strategies for iron-based catalysts supported on clay and zeolite materials, which requires further exploration in subsequent studies.

5.2. Promotion strategies of supported iron-based catalysts

5.2.1. Multi-component active species optimization

As previously discussed, supported iron-based catalysts exhibit excellent catalytic performance on various types of supports. However, their low-temperature activity and resistance to poisoning still require further enhancement. Common modification strategies for iron-based supported catalysts include the incorporation of transition metal or rare earth metal oxides, such as W, Mn, and Ce oxides, which modify the support or regulate the active sites to achieve multi-component active sites optimization. In addition, the synergistic interactions between active sites and active additives can effectively enhance the acidity and redox properties of iron-based supported catalysts, thereby improving the NO_x reduction catalytic performance. Xu *et al.* [99] prepared a series of Fe_2O_3-WO_3/$Ce_xZr_{1-x}O_2$ ($0 \leq x \leq 1$) catalysts with superior low-temperature SCR activity over a wide temperature window and strong resistance to H_2O and SO_2. The significant improvement in catalytic performance is due to the increase of Fe^{3+}, chemisorbed oxygen and active species on the surface *via* adjusting the molar ratio of W/Fe [100]. Lu *et al.* [101] modified Fe_2O_3/activated coke by incorporating Co and Ce oxides, and thoroughly investigated the reaction mechanism. The synthesized 3 % $Fe_{0.6}Co_{0.2}Ce_{0.2}O_{1.57}$/activated coke catalyst demonstrated over 70 % NO_x conversion at 100 °C and achieved more than 90 % NO_x conversion within the 250-350 °C range. Characterization results indicated that the redox cycle involving Fe, Co, and Ce sites, the highly dispersed active components, and the abundant weak acid sites collectively contributed to the enhanced catalytic performance. Based on the above understanding, potential reactions with negative Gibbs free energy in the SCR process have been proposed, including the adsorption of NH_3, the adsorption and oxidation of NO, and the reduction of both NO and NO_2. Along with further studies on the reaction kinetics, they concluded that the modification of $Fe_xCo_yCe_zO_m$ on activated coke could accelerate the release of lattice oxygen, thereby facilitating the "fast SCR" process, which is typically limited by the oxidation of NO (Fig. S13 in Supporting information).

In addition to transition metal or rare earth metal doping, inorganic acid modification has been proved to not only increase

the acidity of supported iron-based catalysts, but also effectively improve the SO_2 tolerance *via* suppressing SO_2 adsorption. Feng *et al.* [102] evaluated the SCR performance and SO_2 resistance of $Fe_2(SO_4)_3/TiO_2$ and $Ce_2(SO_4)_3/TiO_2$ catalysts using the corresponding metal sulfate as precursors. Compared to the $Ce_2(SO_4)_3/TiO_2$ catalyst, $Fe_2(SO_4)_3/TiO_2$ expressed better low temperature SCR activity and tolerance to SO_2, which was resulted from less sulfates formed on the surface. Meanwhile, the presence of NO and O_2 contributed to the decomposition of NH_4HSO_4 on the $Fe_2(SO_4)_3/TiO_2$ catalyst at lower temperatures, which further made $Fe_2(SO_4)_3/TiO_2$ present better SO_2 resistance than $Ce_2(SO_4)_3/TiO_2$. Zhou *et al.* [103] prepared a series of $Fe_2(SO_4)_3/CeO_2$ composite oxide catalysts for NH_3-SCR and demonstrated that the strong reducibility and surface acidity were mainly attributed to the synergistic effect of Fe, Ce and SO_4^{2-} species. In addition, the passivated nitrate generation was inhibited on $Fe_2(SO_4)_3/CeO_2$, accompanied with the adsorption of NH_3 was significantly enhanced, which further ensured the catalyst exhibit excellent catalytic performance and high N_2 selectivity. Meanwhile, the interaction between the sulfate groups and Fe species not only significantly broadened the operating temperature window, but also maintained the excellent stability and NO_x conversion after the introduction of 50 ppm SO_2 and 5 % H_2O.

In addition, we have thoroughly investigated the resistance to alkali metal poisoning of supported iron-based catalysts and unexpectedly observed that SO_2 can induce K migration in alkali metal poisoned $FeVO_4/TiO_2$ catalysts, which greatly alleviated alkali poisoning and successfully restored the NO_x reduction catalytic activity to the initial state [104]. In more details, after sulphation of K-$FeVO_4/TiO_2$ catalysts, SO_4^{2-} preferentially reacting with K_2O to form K_2SO_4, which extended the K-O-Fe and K-O-V bonds, released the active sites poisoned by K_2O and replenished the redox sites, thereby significantly restoring the high SCR activity (Fig. S14 in Supporting information). In addition, the redox capacity of the newly formed active sites could be further enhanced, which also contributed to improved SCR activity at low temperatures. Therefore, in order to effectively avoid alkali metal binding to the active iron sites, we also designed a catalyst consisting of α-Fe_2O_3 crystals embedded in amorphous $FeVO_4$. The embedded α-Fe_2O_3 crystals helped to stabilize the backbone and increase the hydrothermal stability of the catalyst, allowing the catalyst to reach 90 % conversion at 270 °C even after hydrothermal aging at 600 °C and 10 vol% H_2O for 10 h. Furthermore, amorphous $FeVO_4$ provided "ionic channels" that facilitated the migration of alkali metals to internal sacrificial regions, thereby separating them from surface active sites, which imparted excellent resistance to alkali metal poisoning in the catalyst [105].

In summary, the modification of active sites and supports involving multi-metal coupling to achieve the optimization of multi-component active species not only improve the low-temperature catalytic performance of the supported iron-based catalysts, but also effectively enhance the tolerance to H_2O and SO_2. In addition, the electronic effects between multi-metals not only effectively increases the acid sites on the catalyst surface and promotes the adsorption of NH_3, but also increases the content of reactive oxygen species on the catalyst surface, which enhances the redox capacity and the corresponding adsorption and oxidation of NO. All these positive modulations caused by the multi-component active species tuning facilitate the optimization of NO_x reduction catalytic reaction pathways, among which mainly promote the "Fast-SCR" reaction pathway and consequently enhance the low-temperature SCR activity. Finally, the formation of metal acid salts by coupling Fe species and other metal oxides, combined with amorphous structure modulation, effectively prevent the binding of alkali metals with active sites, achieving high NO_x reduction efficiency at low temperatures and imparting excellent resistance to alkali metal poisoning.

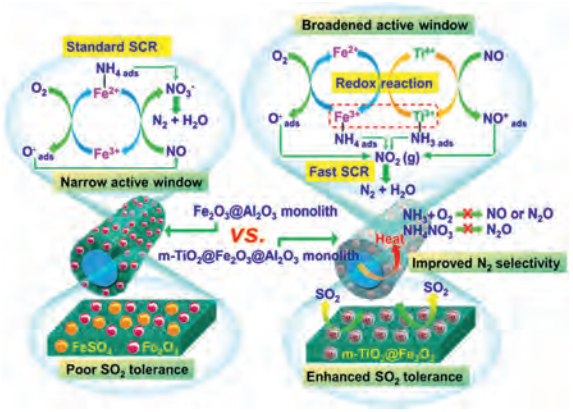


Fig. 11. Schematic illustration of activity/selectivity-promoted and SO_2-resistant mechanisms over the m-TiO_2@Fe_2O_3@Al_2O_3 monolith catalyst for NO_x reduction. Reproduced with permission [107]. Copyright 2019, American Chemical Society.

5.2.2. Core-shell morphology construction

The core-shell structure construction has attracted considerable attention due to its unique structural and chemical properties that always can facilitate most of the heterogeneous catalytic reactions. The heterojunction between the core and shell structure usually can induce unexpected electronic interactions, greatly contributing to the enhancement of catalytic performance. In addition, the core-shell structure commonly isolates the active components of the core with the shell, thus also effectively preventing deactivation of the active components due to various poisoning, in turn increasing the operating durability of most NO_x reduction catalysts.

Basically, we have conducted systematic studies on the structural and morphological modulation of supported iron-based catalysts. We adopted a steam oxidation process to construct mesoporous Al_2O_3 (na-Al_2O_3) nanoarrays *in situ* on the surface of Al mesh (Al-mesh) to form na-Al_2O_3@Al-mesh support. Subsequently, Fe_2O_3 and CeO_2 were anchored onto the na-Al_2O_3@Al-mesh support *via* an impregnation method, and finally the Fe_2O_3-CeO_2@na-Al_2O_3@Al-mesh catalyst was obtained. The strong interaction between Fe_2O_3 and CeO_2 promoted the transfer of electrons from Fe_2O_3 to CeO_2, thereby generating more Fe^{3+} and Ce^{3+} species and accelerating the redox cycle. Moreover, under SO_2 atmosphere, SO_2 preferentially reacted with CeO_2 to form $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$, thereby alleviating the sulphation of active Fe species and enhancing the SO_2 tolerance at low temperatures [106]. Additionally, we synthesized the m-TiO_2@Fe_2O_3@Al_2O_3 catalyst by encapsulating Fe_2O_3 in mesoporous TiO_2 (m-TiO_2@Fe_2O_3) and using a titanate crosslinking agent for one-pot assembly on the custom AlOOH@Al-mesh support. Compared to the adsorption of NO and NH_3, the mesoporous TiO_2 shell (m-TiO_2) in the mesoporous TiO_2@Fe_2O_3@Al_2O_3 composite material showed weaker adsorption of SO_2, along with the deposition of $FeSO_4$ was significantly reduced. The strong electron interaction between HSO_4^- and the Brønsted acid sites from m-TiO_2 destroyed the bond between NH_4^+ and HSO_4^-, which promoted the decomposition of NH_4HSO_4 on m-TiO_2. Therefore, the deposition of $FeSO_4$ and NH_4HSO_4 were both effectively suppressed. At the same time, the electron transfer at the interface of Fe_2O_3 (core) and TiO_2 (shell) accelerated the redox cycle, promoted the "Fast SCR" reaction and widened the low temperature window (Fig. 11) [107].

In previous researches, we found that Fe_2O_3 not only serving as active sites participated in the SCR reaction, but also acting as active promoter protected other active sites from SO_2 poisoning. Therefore, we prepared the Fe_2O_3@CuO_x catalyst by growing Fe_2O_3 nanosheets *in situ* on the CuO_x surface using a hydrothermal method. Compared with the CuO_x catalyst, Fe_2O_3@CuO_x cata-

lysts exhibited a wider operating temperature window and higher SCR activity. In addition, under the conditions of 350 °C and 250 ppm SO_2 involved, the NO_x conversion of Fe_2O_3@CuO_x catalysts could be maintained at about 90 %. This is because Fe_2O_3 not only prevented the formation of $(NH_4)_2SO_4$, but also inhibited the formation of copper sulfate [108]. Furthermore, we prepared V_2O_5-WO_3/Fe_2O_3/TiO_2 microsphere composite oxide catalysts by modifying V_2O_5-WO_3/TiO_2 *via* coating Fe_2O_3 on the surface of TiO_2 microspheres. The modified catalyst showed significant improvements in low-temperature SCR performance and improved SO_2 tolerance, which is attributed to the highly dispersed active species and abundant surface-adsorbed oxygen [109]. Similarly, the halloysite-supported CeO_2-WO_3 catalysts coated with Fe_2O_3 exhibited improved Ce^{3+} ratio and increased content of surface oxygen vacancies. Besides, Fe_2O_3 additives also obviously boosted the content of Brønsted acid sites and active species. More importantly, the Fe_2O_3 outer layer reacted with SO_2 to form $Fe_2(SO_4)_3$, which effectively prevented the interaction of SO_2 with the active CeO_2-WO_3 components, giving the catalyst with excellent SO_2 resistance [110]. The formation of a multi-shell structure resulted in the enhanced adsorption of reactants and increased reactive oxygen species, which contributed to the remarkable denitrification performance.

In summary, through the construction of core-shell morphology, Fe_2O_3, whether serving as the active sites or protective sites, can effectively enhance the electronic interaction between active metal oxides components, adjust the electronic state of active sites, thus significantly improving the NO_x reduction catalytic activity. In addition, the metal oxide shell can also reduce SO_2 adsorption or act as sacrificial sites by preferentially binding SO_2, thereby protecting the core active sites from poisoning, resulting in excellent SO_2 tolerance of the supporting iron-based catalysts.

6. Summary and perspective

In summary, iron-based metal oxide catalysts have received widespread attention due to their excellent performance at medium to high temperatures and feasible industrial efficiency. However, several shortcomings including poor low-temperature performance, narrow operating temperature windows, as well as insufficient resistance to SO_2/H_2O and alkali metal poisoning still further limit the application of iron-based metal oxide catalysts. By reviewing plenty of related studies, we summarize the catalytic properties and structural characteristics for different types of iron-based metal oxide catalysts, and further conclude the promotional strategies of catalytic activity improvement and anti-poisoning performance enhancement over iron-based metal oxide catalysts for NO_x reduction as follows:

(1) Fe_2O_3-based catalysts exhibit excellent catalytic performance at medium to high temperatures, but their relatively poor low-temperature SCR activity requires significant improvement. It has been concluded that the low temperature catalytic activity can be significantly improved by modulating the crystal phase structure to expose highly active crystalline surfaces (such as (110) and (100)). In addition, interfacial effects are established through specific crystal morphology adjustment to promote electron transfer between active metals and facilitate the adsorption activation of NH_3 and NO. Finally, the utilization of heteropolyacids to realize surface grafting modification or doping oxidizing metals on the catalyst surface to realize multi-metal synergistic modulation both effectively inhibit the conversion of γ-Fe_2O_3 to α-Fe_2O_3, which not only improves the low temperature activity but also improves the catalyst resistance to SO_2/H_2O to some extent.

(2) In terms of iron-based composite oxides catalysts, the interactions between Fe_2O_3 and other components endow Fe_2O_3 superior capacity in improving the NO_x reduction catalytic activity, especially within the medium and high temperature range, whether Fe_2O_3 species are served as active components or as promoted additives. The relatively poor low-temperature catalytic activity can be further improved by adjusting the synthesis method and optimizing the active site distribution without changing the catalyst components. In addition, doping other metal oxides to driven the oxidizing metal interaction is also considered as one of the effective strategies to improve the low-temperature catalytic activity of iron-based composite oxides catalysts. By establishing strong metal interactions between Fe species and other metal oxides such as W, Ce, Mn oxides, neighborhood electron modulation can be achieved, which can increase the redox capacity of catalysts and improve the tolerance of the iron-based composite oxides catalysts to SO_2/H_2O.

(3) Iron-based acidic salt catalysts can be commonly classified into iron-based metal acidic salt catalysts and iron-based non-metal acidic salt catalysts. Due to higher acid content and better redox properties, iron-based acid salt catalysts usually demonstrate superior NO_x reduction catalytic performance. To further enhance the low-temperature catalytic activity and broaden the operating temperature window, the electron-induced effect modulation can be realized by doping the catalysts with additional metals such as Mn and Ce, which can significantly increase the redox capacity of catalysts. In addition, coupling with acidic metal oxides or inorganic acids can greatly increase the surface acidity and promote the enrichment of surface acid sites of iron-based acid salt catalysts, which further disperse the active iron sites and promote the adsorption activation of NH_3 as well. Similarly, by coupling with strong acidic supports (such as TiO_2, CeO_2), the NH_3 adsorption and activation can be further enhanced and the active iron sites also can be further dispersed to maintain higher catalytic activity and operating stability. In addition, alkali metal resistance can be significantly improved by modifying the active sites with sulfuric acid or phosphoric acid, due to the construction of sacrificial sites by sulfuric acid and phosphoric acid groups, which preferentially interact with alkali metals and release the active iron sites.

(4) Supported iron-based catalysts typically exhibit excellent NO_x reduction catalytic activity and thermal stability, which is mainly due to the high surface area of various supports promote higher dispersion of active sites. In addition, appropriate modification of the active sites and support materials allow multi-component active species optimization is realized *via* coupling multi-metals (such as Mn, Ce, Zr), which improves the catalytic activity and tolerance to H_2O and SO_2 as well. In this process, the oxidative properties of supported iron-based catalysts are enhanced to promote NO adsorption and oxidation to optimize the catalytic reaction pathways, which results in a significant improvement in the low temperature catalytic activity. In order to improve the anti-poisoning ability of supported iron-based catalysts, the core-shell structure construction or amorphous structure modulation could effectively reduce the attachment of poisons on active sites or adjust the binding position of poisons on various sacrificial sites, thus protecting the active sites from being impaired and greatly improving the ability to resist sulfur dioxide and alkali metal poisoning.

This review summarizes the development, challenges and modification strategies of various types of iron-based metal oxide catalysts, providing researchers with insights into different promotional approaches to realize catalytic activity improvement and anti-poisoning performance enhancement over iron-based metal oxide catalysts for NO_x reduction. Therefore, doping with metal oxides or coupling with metal oxide supports to establish strong metal-support interactions can effectively improve NO_x conversion efficiency and extend catalyst lifetime. In addition, modification with low-cost metals or non-metallic elements allows electron-induced regulation and optimization of active site distribution to improve catalytic performance while reducing industrial costs. However, the discussion on the improvement of the sintering resistance of iron-based catalysts and the related optimization strate-

gies is still limited. Therefore, improving the sintering resistance and NO_x conversion efficiency of catalysts, extending their operating life while reducing industrial costs to achieve economic feasibility remain key challenges for the industrialization of iron-based catalysts. However, the meticulous understanding of specific catalytic mechanisms of Fe active sites regarding to improving catalytic activity and anti-poisoning ability at the atomic level remains unclear, particularly with regard to their dynamic changes during the NO_x reduction reaction and anti-poisoning process. This can be further explored using advanced *in situ* and operando characterization techniques to investigate the dynamic changes of active sites during the reaction process, particularly under the influence of various poisons, such as the evolution of the coordination environment of Fe atoms, the formation of reaction intermediates, and changes in the catalyst structure. In addition, machine learning can also be used to predict the optimal Fe atomic coordination environment, catalyst morphology, and exposed crystal facets. This will aid researchers in formulating targeted strategies to improve the catalytic activity and poisoning resistance to multiple poisons of iron-based metal oxide catalysts. In addition, due to the complexity of flue gases in practical operating conditions, multiple poisons including SO_2, HCl, HF, phosphates, alkali metal, alkaline earth metal as well as heavy metals will affect iron-based catalysts simultaneously. Therefore, probing into the complex interactions between different poisons and analyzing their superimposed inhibitory effects on catalysts will help researchers to propose targeted solutions for the design of multifunctional catalyst structures, such as the use of porous supports to physically isolate the toxicants or the introduction of multiple active components to individually counteract the different poisons, thus addressing the severe deactivation issues that most of NO_x reduction catalysts encountered. Eventually, due to the advantages of adjustable redox properties, abundant surface acidity, and flexible structural design space, iron-based metal oxide catalysts can be adopted to attempt the multi-pollutants elimination that require hierarchical surface acidity and redox properties, such as the synergistic elimination of NO_x and volatile organic compounds (VOCs) remain in the flue gas control among most non-electric industries including waste incineration plants, biomass burning furnaces, steel, cement as well as architectural material industries. This requires researchers to pay more attention to the catalytic performance and reaction mechanisms of iron-based catalysts in different atmospheres. Therefore, in order to adapt to the variations of different industrial flue gas compositions, it is necessary to combine experimental characterization with theoretical calculations, and to develop advanced catalyst systems such as core-shell structures and multistage pores through hierarchical acid-redox design and dynamic anti-poisoning interface construction. This will promote the large-scale industrial application of iron-based catalysts.

Declaration of competing interest

All authors declare that there are no conflicts of interest, financial or otherwise in this work, and there are no other relationships or activities that can appear to have influenced the submitted work.

CRediT authorship contribution statement

Zaisheng Jin: Writing – original draft, Methodology, Investigation. **Fuli Wang:** Writing – review & editing, Methodology. **Yongjie Shen:** Writing – review & editing, Methodology. **Xiaonan Hu:** Writing – review & editing. **Yanqi Chen:** Methodology. **Jin Zhang:** Investigation. **Ming Xie:** Writing – review & editing. **Penglu Wang:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Dengsong Zhang:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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Supplementary materials

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References

[1] C. Dong, J. Yao, J. Shi, et al., Fuel 381 (2025) 133311–133336.
[2] D. Ye, S. Gao, J. Feng, X. Wang, Mol. Catal. 549 (2023) 113516.
[3] F. Wang, P. Wang, J. Zhang, et al., Chin. Chem. Lett. 35 (2024) 108800–108811.
[4] C. Hu, C. Liu, K. Du, et al., J. Environ. Chem. Eng. 11 (2023) 110440–110448.
[5] X. Mou, B. Zhang, Y. Li, et al., Angew. Chem. Int. Ed. 51 (2012) 2989–2993.
[6] H. Wang, Z. Qu, H. Xie, et al., J. Catal. 338 (2016) 56–67.
[7] Z. Liu, H. Su, B. Chen, et al., Chem. Eng. J. 299 (2016) 255–262.
[8] S. Wu, X. Yao, L. Zhang, et al., Chem. Commun. 51 (2015) 3470–3473.
[9] S. Yang, S. Xiong, Y. Liao, et al., Environ. Sci. Technol. 48 (2014) 10354–10362.
[10] S. Xiong, Y. Liao, X. Xiao, et al., Catal. Sci. Technol. 5 (2015) 2132–2140.
[11] F. Liu, H. He, Z. Lian, et al., J. Catal. 307 (2013) 340–351.
[12] L. Ma, J. Li, R. Ke, L. Fu, J. Phys. Chem. C 115 (2011) 7603–7612.
[13] Y. Piao, J. Kim, H.B. Na, et al., Nat. Mater. 7 (2008) 242–247.
[14] L. Machala, J.i. Tuček, R. Zbořil, Chem. Mater. 23 (2011) 3255–3272.
[15] X. Mou, Y. Li, B. Zhang, et al., Eur. J. Inorg. Chem. 2012 (2012) 2684–2690.
[16] X. Wang, K. Gui, J. Environ. Sci. 25 (2013) 2469–2475.
[17] H. Liu, Z. Zhang, Q. Li, et al., Aerosol Air Qual. Res. 17 (2017) 1898–1908.
[18] Z. Gong, S. Niu, Y. Zhang, C. Lu, Mater. Res. Bull. 123 (2020) 110693–110700.
[19] W. Teng, J. Li, X. Dai, et al., Appl. Surf. Sci. 647 (2024) 158938–158951.
[20] X. Wang, X. Zhang, X. Cao, et al., Sep. Purif. Technol. 357 (2025) 130235–130248.
[21] M. Gao, G. He, W. Zhang, et al., Environ. Sci. Technol. 55 (2021) 10967–10974.
[22] C. Liu, S. Yang, L. Ma, et al., Catal. Lett. 143 (2013) 697–704.
[23] W. Qu, Y. Chen, Z. Huang, et al., Environ. Sci. Technol. Lett. 4 (2017) 246–250.
[24] Y. Zhou, X. Yang, C. Gong, et al., Chem. Eng. J. 475 (2023) 146198–146233.
[25] W. Zhang, X. Shi, Z. Yan, et al., ACS Catal. 11 (2021) 9825–9836.
[26] H. Rahman, S. Nakashima, J. Magn. Magn. Mater. 596 (2024) 171940.
[27] H. Cui, W. Ren, W. Wang, J. Sol-Gel. Sci. Technol. 54 (2010) 37–41.
[28] J. Lai, K.V.P.M. Shafi, K. Loos, et al., J. Am. Chem. Soc. 125 (2003) 11470–11471.
[29] D. Mo, Q. Qin, C. Huang, et al., Appl. Catal. B: Environ. Energy 349 (2024) 123869–123882.
[30] Y. Geng, S. Xiong, B. Li, et al., Ind. Eng. Chem. Res. 57 (2018) 13661–13670.
[31] Z. Ren, Y. Teng, L. Zhao, R. Wang, Catal. Today. 297 (2017) 36–45.
[32] Z. Ren, H. Fan, R. Wang, Catal. Commun. 100 (2017) 71–75.
[33] Y. Li, Y. Wan, Y. Li, et al., ACS Appl. Mater. Interfaces 8 (2016) 5224–5233.
[34] J. Zhang, Z. Huang, Y. Du, et al., ACS Appl. Energy Mater. 1 (2018) 2385–2391.
[35] Z. Huang, J. Zhang, Y. Du, et al., ChemCatChem 11 (2019) 3035–3041.
[36] C. Shao, X. Liu, D. Meng, et al., RSC Adv. 6 (2016) 66169–66179.
[37] C. Wang, S. Yang, H. Chang, et al., J. Mol. Catal. A: Chem. 376 (2013) 13–21.
[38] Y. Wei, P. Liang, Y. Li, et al., J. Environ. Chem. Eng. 10 (2022) 107772–107782.
[39] S. Ma, X. Zhao, Y. Li, et al., Appl. Catal. B: Environ Energy 248 (2019) 226–238.
[40] H. Wang, P. Ning, Y. Zhang, et al., J. Hazard. Mater. 388 (2020) 121812–121823.
[41] C. Li, Z. Huang, Y. Chen, et al., ChemCatChem 10 (2018) 3990–3994.
[42] S. Yang, J. Li, C. Wang, et al., Appl. Catal. B: Environ. Energy 117-118 (2012) 73–80.
[43] Z. Chen, F. Wang, H. Li, et al., Ind. Eng. Chem. Res. 51 (2011) 202–212.
[44] W. Sun, X. Li, Q. Zhao, et al., Catal. Lett. 148 (2018) 227–234.
[45] M. Guo, P. Zhao, Q. Liu, et al., ChemCatChem 11 (2019) 4954–4965.
[46] H. Hu, K. Zha, H. Li, et al., Appl. Surf. Sci. 387 (2016) 921–928.
[47] X. Zhibo, L. Chunmei, G. Dongxu, et al., J. Chem. Technol. Biotechnol. 88 (2013) 1258–1265.
[48] R. Wang, X. Wu, C. Zou, et al., Catalysts 8 (2018) 384–396.
[49] S. Chen, Q. Yan, C. Zhang, Q. Wang, Catal. Today 327 (2019) 81–89.
[50] S. Zhan, D. Zhu, S. Yang, et al., J. Sol-Gel Sci. Technol. 73 (2015) 443–451.
[51] K. Zhao, W. Han, Z. Tang, et al., Catal. Surv. Asia 22 (2018) 20–30.
[52] K. Cheng, B. Liu, W. Song, et al., Ind. Eng. Chem. Res. 57 (2018) 7802–7810.
[53] N. Fang, J. Guo, S. Shu, et al., Chem. Eng. J. 325 (2017) 114–123.
[54] L. Yuan, P. Hu, B. Hu, et al., J. Fuel Chem. Technol. 51 (2023) 1843–1855.
[55] W. Chen, S. Yang, H. Liu, et al., Environ. Sci. Technol. 56 (2022) 10442–10453.
[56] L. Song, H. Yue, K. Ma, et al., Ind. Eng. Chem. Res. 59 (2020) 8164–8173.
[57] X. Liu, P. Wang, Y. Shen, et al., Environ. Sci. Technol. 56 (2022) 11646–11656.
[58] M. Lyu, J. Zou, X. Liu, et al., Catal. Sci. Technol. 12 (2022) 4020–4031.

[59] Z. Shen, P. Wang, X. Hu, et al., Environ. Sci. Technol. 57 (2023) 14472–14481.
[60] K. Oshiro, M. Gao, L. Han, et al., J. Phys. Chem. C 127 (2023) 18914–18925.
[61] F. Liu, H. He, C. Zhang, Chem. Commun. (2008) 2043–2045.
[62] F. Liu, Y. Yu, W. Shan, H. He, Sci. Sin. Chim. 42 (2012) 446–468.
[63] F. Liu, H. He, C. Zhang, et al., Appl. Catal. B: Environ. Energy 96 (2010) 408–420.
[64] F. Liu, H. He, C. Zhang, et al., Catal. Today 175 (2011) 18–25.
[65] F. Liu, K. Asakura, P. Xie, et al., Catal. Today. 201 (2013) 131–138.
[66] F. Liu, H. He, L. Xie, ChemCatChem 5 (2013) 3760–3769.
[67] Q. Zhang, Y. Zhang, T. Zhang, et al., Appl. Surf. Sci. 503 (2020) 144190–144202.
[68] T. Zhang, Y. Zhang, P. Ning, et al., Appl. Surf. Sci. 538 (2021) 147999–148012.
[69] P. Zhang, D. Li, Catal. Lett. 144 (2014) 959–963.
[70] J. Mu, X. Li, W. Sun, et al., ACS Catal. 8 (2018) 6760–6774.
[71] Y. Yu, C. Chen, M. Ma, et al., Chem. Eng. J. 361 (2019) 820–829.
[72] F. Liu, H. He, Y. Ding, C. Zhang, Appl. Catal. B: Environ. Energy 93 (2009) 194–204.
[73] A. Karami, V. Salehi, J. Catal. 292 (2012) 32–43.
[74] W. Tan, S. Xie, W. Shan, et al., Front. Environ. Sci. 16 (2022) 60–73.
[75] L. Kang, L. Han, P. Wang, et al., Environ. Sci. Technol. 54 (2020) 14066–14075.
[76] X. Li, K. Li, Y. Peng, et al., Chem. Eng. J. 347 (2018) 173–183.
[77] H. Wang, Z. Qu, S. Dong, et al., Environ. Sci. Technol. 50 (2016) 13511–13519.
[78] H. Wang, Z. Qu, S. Dong, C. Tang, ACS Appl. Mater. Interfaces 9 (2017) 7017–7028.
[79] L. Ding, H. Zhao, K. Cheng, et al., J. Iron. Steel Res. Int. 31 (2024) 2110–2121.
[80] M. Casanova, L. Nodari, A. Sagar, et al., Appl. Catal. B: Environ. Energy 176-177 (2015) 699–708.
[81] A. Marberger, M. Elsener, D. Ferri, et al., ACS Catal. 5 (2015) 4180–4188.
[82] C. Feng, P. Wang, X. Liu, et al., Environ. Sci. Technol. 55 (2021) 11255–11264.
[83] Y. Li, S. Cai, P. Wang, et al., Environ. Sci. Technol. 55 (2021) 9276.
[84] T. Boningari, D.K. Pappas, P.G. Smirniotis, J. Catal. 365 (2018) 320–333.
[85] J. Liu, J. Meeprasert, S. Namuangruk, et al., J. Phys. Chem. C 121 (2017) 4970–4979.
[86] J. Han, J. Meeprasert, P. Maitarad, et al., J. Phys. Chem. C 120 (2016) 1523–1533.
[87] J. Zhang, Z. Huang, Y. Du, et al., Chem. Eng. J. 381 (2020) 122668–122679.
[88] Y. Chen, C. Li, J. Chen, X. Tang, Environ. Sci. Technol. 52 (2018) 11796–11802.
[89] Y. Chen, H. Yan, W. Teng, et al., Fuel 337 (2023) 127210–127223.
[90] J. Han, D. Zhang, P. Maitarad, et al., Catal. Sci. Technol. 5 (2015) 438–446.
[91] Z. Yang, B. Huang, G. Zhang, et al., J. Wuhan Univ. Technol. 38 (2023) 475–484.
[92] P. Li, Y. Huang, S. Li, M. Liu, Sep. Purif. Technol. 352 (2025) 128210–128224.
[93] S. Li, Y. Huang, H. Zhu, et al., Fuel 341 (2023) 127716–127726.
[94] Y. Tang, Y. Tao, J. Wu, et al., J. Mater. Res. 34 (2019) 1188–1199.
[95] X. Wang, J. Zhou, T. Zhao, et al., J Environ Sci. (China) 88 (2020) 237–247.
[96] G. Li, B. Wang, Z. Wang, et al., J. Phys. Chem. C 122 (2018) 20210–20231.
[97] X. Zhang, P. Wang, X. Wu, et al., Catal. Commun. 83 (2016) 18–21.
[98] B.S. Agnieszka Szymaszek, Monika Motak, Physicochem. Probl. Miner. Process. 55 (2019) 1429–1441.
[99] H. Xu, Y. Cao, Y. Wang, et al., Chin. Sci. Bull. 59 (2014) 3956–3965.
[100] H. Xu, Y. Li, B. Xu, et al., J. Ind. Eng. Chem. 36 (2016) 334–345.
[101] P. Lu, R. Li, Y. Xing, et al., Fuel 233 (2018) 188–199.
[102] C. Feng, L. Han, P. Wang, et al., J. Environ. Sci. (China) 111 (2022) 340–350.
[103] Z. Zhou, W. Li, Z. Liu, Ind. Eng. Chem. Res. 60 (2021) 15472–15478.
[104] Z. Si, Y. Shen, J. He, et al., Environ. Sci. Technol. 56 (2022) 605.
[105] J. Deng, S. Cai, M. Gao, et al., ACS Catal. 13 (2023) 12363–12373.
[106] L. Han, M. Gao, C. Feng, et al., Environ. Sci. Technol. 53 (2019) 5946–5956.
[107] L. Han, M. Gao, J.Y. Hasegawa, et al., Environ. Sci. Technol. 53 (2019) 6462–6473.
[108] C. Fang, L. Shi, H. Hu, et al., RSC Adv. 5 (2015) 11013–11022.
[109] R. Gao, D. Zhang, X. Liu, et al., Catal. Sci. Technol. 3 (2013) 191–199.
[110] L. Kang, L. Han, J. He, et al., Environ. Sci. Technol. 53 (2019) 938.