

Review of Researches on SCR Catalyst with Low Temperature and high Sulfur Tolerance and Theoretical Design

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Abstract. Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) using ammonia (NH₃) is currently the main technology for flue gas denitration. However, the currently widely used commercial catalysts (such as V₂O₅-WO₃ / TiO₂, V₂O₅-MoO₃ / TiO₂, etc.) have the disadvantages of high operating temperature, narrow active temperature window, and high catalytic cost. Therefore, in recent years, researchers have devoted themselves to the development of low-cost and efficient low-temperature SCR catalytic materials. This paper summarizes the research progress of low-temperature (less than 250 °C) selective catalytic reduction of NO_x by unsupported metal oxide catalysts, supported metal oxide catalysts, precious metals, and molecular sieve catalysts. Among them, manganese-based catalysts show good low-temperature selectivity and stability, and have good application prospects. Finally, the research directions of manganese low temperature SCR catalysts are prospected and theoretically designed based on the existing problems.

1. Introduction

Nitric oxide (NO_x) refers to compounds composed of nitrogen and oxygen. Common NO_x include N₂O, NO, NO₂, N₂O₃ and N₂O₅. NO and NO_x are common atmospheric pollutants. NO_x has the following three aspects of harms, which are harms to physical health, damages of acid rains to crops, soils and forest, and atmospheric damages.

90~95% of NO_x in atmosphere comes from emission of industrial factories. In the following text, statistics on the proportions of NO₂ cities with different concentrations in the recent 6 years (Figure 1) [1], data of national NO_x emission in the recent 7 years (Figure 2) [2], annual average concentrations of NO₂ in key cities in the recent 10 years (Figure 3) [3] and NO_x emission of national key industries (Figure4) [3] were made. According to the variation trend, we found that China has made great efforts to reduce NO_x emission and achieved significant effect. However, how to decrease NO_x emission from industrial factors is still the key research hotspot in future.

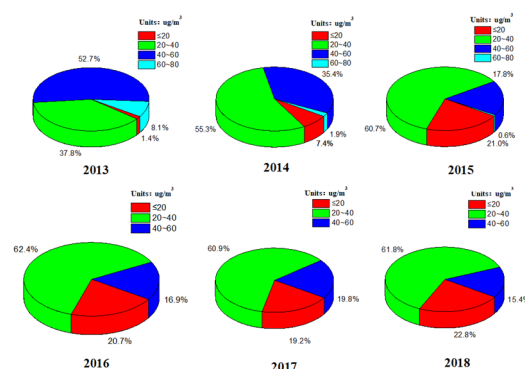


Figure 1. Proportion of NO₂ cities with different concentrations in recent six years

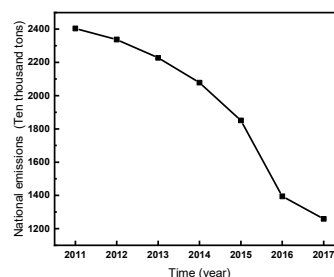


Figure 2. Data of national NO_x emission in the past seven years

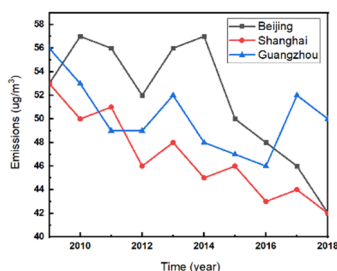


Figure 3. Annual average concentration of NO₂ in recent ten years in some key cities

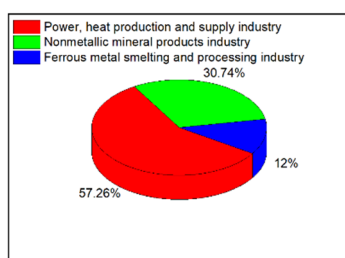


Figure 4. NO_x emission of national key industries

2. Conclusions and reviews of researches on low-temperature SCR catalysts

Selective catalytic reduction (SCR) reaction is the denitration reaction which is applied relatively widely. At present, vanadium tungsten titanium catalyst (V₂O₅-WO₃(MoO₃)/TiO₂) is the SCR catalyst which is applied the mostly. The activity window of vanadium tungsten titanium is 300~400°C and it is put at the tail gas. Existing studies on SCR catalyst are shown in Figure 5, where precious metals include Pt, Pb and Ag [4-7] and transition metal oxide catalysts refer to Mn, Fe, V, Cu, Cr and Co [8-14].

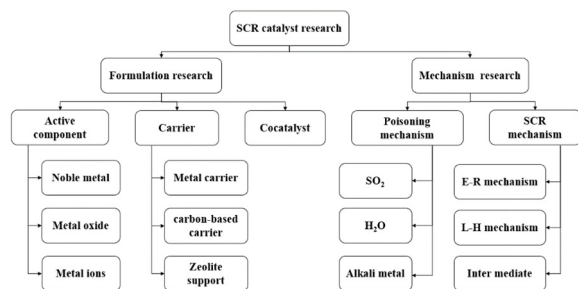
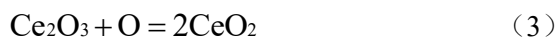
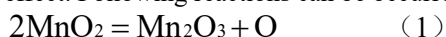


Figure 5. SCR catalyst research

2.1. Carrier-free metallic oxide catalysts

Carrier-free metallic oxide catalysts refer to Mn, Fe, V, Cu, Cr, Co, etc. [8-14]. Take Mn for example. It can be divided into two types. One is the single metallic oxide catalyst MnO₂ which has good sulfur resistance under low temperature. However, selectivity of N₂ is relatively poor. The other is the multi-component metallic oxide catalyst CeO₂-MnO₂, where Ce and Mn have synergic effect. Following reactions can be occurred:



Therefore, the supported SCR catalysts which use transition metallic oxide as the activity center are the key development objects in future.

2.2. The supported metallic oxide catalysts

Common supported metallic oxide catalysts include Al₂O₃, TiO₂, carbon base, molecular sieve, MnO₂, etc. Singoredjo et al. [15] prepared M nitric oxides/ Al₂O₃ catalyst by using manganese acetate and manganous nitrate as the precursors for the first time, and found that the M nitric oxide prepared by using manganese acetate as the precursor had better dispersity and stronger denitration activity. Cao et al. [16-18] modified the highly dispersed Zr, Ag and Fe in Mn-Ce/γ-Al₂O₃, finding that specific surface area of γ-Al₂O₃ is the key to improve denitration activity. As a good carrier, Al₂O₃ can promote denitration of SCR, but it has poor resistance to SO₂, thus restricting its applications in coal-fired boiler. Although the acidity of TiO₂ is lower than that of Al₂O₃, TiO₂ can be dispersed in metallic active components well, promote decomposition of surface sulfates and provide good SO₂ resistance. Therefore, TiO₂ is one of carriers of the NH₃-SCR catalyst. At present, V₂O₅-WO₃/TiO₂ is the most mature commercial catalyst and it has relatively high activity and SO₂ resistance. Jin et al. [19] prepared Mn-Ce supported catalyst by using Al₂O₃ and TiO₂ as the carrier. They found that TiO₂ carrier presented better activity under 150°C, but it was the Al₂O₃ carrier presented better activity after 220°C. Combining with TPD results, the surface of Mn-Ce/TiO₂ is more occupied by Lewis acid sites and reactions are implemented through the E-R mechanism. On contrary, the surface of Mn-Ce/Al₂O₃ is mainly occupied by Brønsted acid sites. These two catalysts follow different reaction paths. However, specific surface area of ordinary TiO₂ is relatively low and active components are difficult to be used fully. Besides, SCR catalyst based on TiO₂ shows moderate performance under low temperature. Gálvez et al. [20] introduced in few vanadium compounds to the surface of active carbon and the acid site on the loaded active carbon surface is increased. The conversion rate of NO_x was 40% at 125°C and it was further increased to as high as 80% at 200°C, which was far higher than the adsorption efficiency of pure active carbon (43%). Guo et al. [21] studied properties of oxygen-containing functions on coal-based active carbon surface in SCR reaction and found that carboxyls, anhydrides and phenolic groups on active carbon surface enhanced adsorption of NH₃, thus promoting conversion rate of NO_x. Moreover, carbon nanotubes (CNTs), a kind of special ordered material, are also tried to be used as the carrier of SCR catalyst because of their unique nanostructure and electrical properties. Su et al. [22] found that M nitric oxide (Mn-in-CNTs) which was restricted in carbon nanotube channels had higher capacity of oxygen supply and NO adsorption. The Mn-in-CNTs have stronger NH₃-SCR

activity than the catalyst where Mn nitric oxide is anchored onto external surface of CNTs (Mn-out-CNTs).

Molecular sieve is a type of porous material formed by silicon and aluminum tetrahedron. It has very high specific surface, thermal stability and surface acidity, and it is one of high-quality carriers for supported SCR catalyst. Currently, ZSM-5, SPAO-34 and SSZ-13 are common molecular sieves. In 1989, Iwamoto et al. [23] discovered for the first time that Cu²⁺ exchanged ZSM-5 molecular sieve could catalyze decomposition of NO and nitric oxide conversion efficiency of Cu-ZSM-5 with 73% exchange could reach 85% at 550°C. Choong-KilSeo et al. [24] studied influences of ZrO₂ adulteration on denitration activity of Cu-ZSM-5, finding that the NO_x conversion rate of Cu-ZSM-5-ZrO₂(2wt%) was 10%~20% higher than that of Cu-ZSM-5. Ford Company [25] compared thermal stability of metal molecular sieve catalyst and vanadium-based catalyst. After keeping under 670°C for 64h, it was found that thermal stability of the metallic molecular sieve catalyst was attributed to the vanadium base. Meanwhile, the reaction temperature of Fe molecular sieve was lower compared to the Cu molecular sieve. Previous studies all focus on Fe and Cu. The Fe-Mn/ZSM-5 prepared by Mu et al. [26] showed relatively high NH₃-SCR activity during 100~300°C. Through an in-situ infrared test, it found that appropriate Mn⁴⁺/Mn³⁺ and Fe³⁺/Fe²⁺ promoted generation of linear nitrite and monodentate nitrate which were in favor of reactions, thus improving low-temperature activity of NH₃-SCR. Du et al. [27] prepared Fe-ZSM-5@silicalite-1 with core-shell structure through the secondary hydrothermal technique and the Fe-ZSM-5 after modification of silicalite-1 shell improved the SCR activity and water resistance. These were mainly attributed to NO_x adsorption and the extremely good hydrophobicity of the silicalite-1 shell.

To sum up, traditional metal carriers have small specific area, easy deactivation and easy toxicity due to limitations of their physical and chemical properties. Al₂O₃ catalyst is easy to react with water due to the existence of Al atoms, which restricts its applications in humid environment. Carbon-based material has developed diameters and rich functional groups, but it has poor thermal stability. Therefore, these materials are difficult to realize industrialized applications. Other nanomaterials, such as active carbon fiber, CNTs and graphene, have specific structures, specific pore diameters and good performance. However, they are still in the laboratory level for the high preparation cost. Molecular sieve not only is equipped with rich specific surface areas, pore diameter structures, good thermal stability and high mechanical strength, but also shows outstanding adsorption effect to micromolecules. Hence, molecular sieve has a promising application prospect as a supported catalyst.

3. Mn-based catalyst

3.1 Introduction to the MnO₂ structure

MnO₂ is the sum of a type of compounds. It is embedded with potassium ions and has more than 10 crystalline phases [28].

The microstructures of β-MnO₂ which are observed along the Z axis are shown in Figure 6. In Figure 6(a), a manganese atom is connected with 6 oxygen atoms, forming an octahedron with group symmetry. The sp² hybridization of β-MnO₂ is shown in Figure 6(b), which makes the pore passages dispersed. Hence, β-MnO₂ cannot be used as a catalyst.

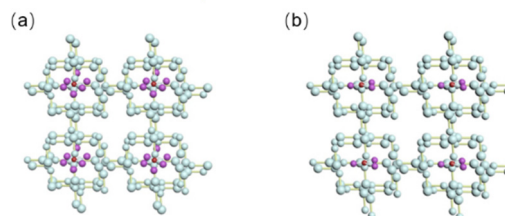


Figure 6. Microstructure of β-MnO₂

The microstructure of α-MnO₂(OMS-2) is shown in Figure 7, which includes skeleton, sp² hybridization and sp³ hybridization. The stacking modes of α-MnO₂ and β-MnO₂ atoms are different. The former one combines pore passages to be quadruple of the original structure. α-MnO₂ and β-MnO₂ are tetrahedral and octahedral structures, which are stacked along the Z axis. They grow along one direction during synthesis and nanowires are generated [29].

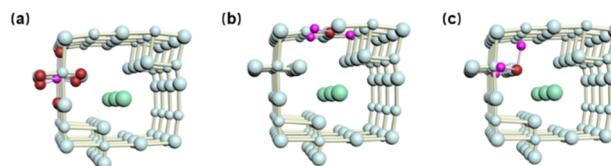


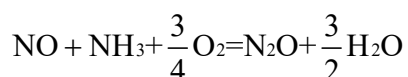
Figure 7. Microstructure of α-MnO₂

In a word, we have to determine where are active sites of α-MnO₂. Therefore, we have to accomplish the surface analysis of α-MnO₂ to disclose the catalysis principle.

3.2. Research review on MnO₂ low-temperature SCR catalyst

MnO₂ has been widely applied due to the excellent catalysis performance. According to experimental results, the MnO₂/CeO₂ catalyst has extremely high NO catalytic performances and even 100% conversion rate can be achieved at 50°C [30]. This almost realizes NO_x removal under room temperature. Moreover, performances of the MnO₂/CeO₂ catalyst are improved significantly by adjusting the proportion of Mn and Ce. This study can be viewed as a typical representative for MnO₂ catalytic denitration.

MnO₂ has following two disadvantages. One is excessive strong oxidability. The selectivity of N₂ is low and some by-products are N₂O. Under normal conditions, N₂O mainly comes from the reaction between NH₃ and NO. Combining with previous studies, there might be a decomposition route of NH₄NO₃ [31,32].



Direct oxidation of NH₃ is accompanied under high
 $2\text{NH}_3 + 2\text{O}_2 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$

The second is poor sulfur resistance of MnO₂. It can be seen from Figure 8 that the catalyst loses activity completely after about 4h accession under the atmospheric environment of 600ppm SO₂ and 5% H₂O. Even when SO₂ and H₂O are cut off, the catalyst still cannot return to the previous conversion rate. According to experimental results, the Mn-based catalysts have extremely poor sulfur resistance and they cause irreversible toxicity rather than simple absorption toxicity. This is one disadvantage of Mn-based catalysts. Therefore, current studies shall focus on improvement of sulfur resistance and selectivity, and providing a new idea to improve sulfur resistance.

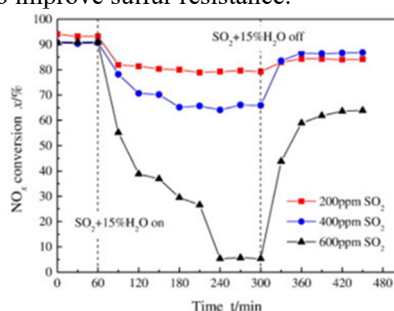


Figure 8. NO conversion rate of different Fe-Ho-Mn/TiO₂ under the atmospheric contents of SO₂ and H₂O [33]

4. Research conclusions on sulfur resistance improvement

The mechanism of toxication of SO₂ under high temperature is completely different from those of ordinary molecules. Different from ordinary materials, SO₂ doesn't generate activity inhibition of catalyst due to competitive adsorption. This is mainly because SO₂ has reaction activity and it often react with the catalyst or its reactants. For SCR, SO₂ serves for different roles in the high-temperature interval and low-temperature interval. SO₂ might promote the reaction in the high-temperature interval [34]. This can be explained as follows. NH₃ adsorption under high temperature is very weak and it often has desorption, making it difficult to participate in the reaction [35]. Therefore, SCR catalyst requires certain acidity under high temperature to stabilize the adsorbed NH₃. B acid sites will be generated on the catalyst surface under the existence of water vapor and sulfur, thus facilitating NH₃ adsorption and increase activity of the catalyst. According to the study of Liu et al. [36], SO₄²⁻ can appear as strong B acid. As a result, we conclude that appropriate access of SO₂ or sulfating of catalyst is beneficial. Therefore, existence of SO₂ under high temperature is generally not a significant problem.

Under low temperature, SO₂ presents toxic properties of catalyst. This has different explanations at present. When the catalyst contains SO₂, NH₄HSO₄ is generated on the catalyst surface, accompanied with catalyst

$$(4) \Delta H = -325\text{KJ/mol}, \Delta G = -309\text{KJ/mol}$$

temperature.

$$(5) \Delta H = -511\text{KJ/mol}, \Delta G = -549\text{KJ/mol}$$

toxicity caused by metal sulfate. NH₄HSO₄ is covered on surface of the catalyst, thus separating activity centers on catalyst surface from reactants. Hence, the catalyst loses activity. Metal sulfate often can stabilize valence-changing elements of the catalyst into the low-valence state to separate them from SCR reduction and thereby trigger inactivation. In a word, it takes a very long period to observe significant inactivation of catalyst under low SO₂. This property brings a great challenge to study sulfur resistance of catalyst and it is easy to cause wrong understanding and wrong explanation of experimental data. As a result, improving sulfur resistance of catalyst is a very challenging study.

On this basis, the following schemes to improve sulfur resistance are proposed through literature review: (1) increasing acid sites. Since SO₂ is a typical acid molecule, attentions can be paid to acidizing of catalyst surface to improve the sulfur resistance. Besides, SCR catalysis requires participation of certain acid sites in the reaction, the performance of catalyst can be improved by introducing in the acid sites. (2) Introducing in sacrificial agent. Catalyst can be protected by using some materials as the sacrificial agent to react with SO₂ firstly. Take vanadium tungsten titanium for example, Ti is very easy to be the center of sulfate. We think Ce can be used as the sacrificial agent. There are three associated studies. One is to add Ce into Mn-based and Ti-based catalysts, which can increase sulfur resistance significantly. The second is to add Ce into FeM nitric oxide to increase sulfur resistance significantly. The third one is add Ce to protect active sites and the sulfur resistance is increased significantly. As a result, adding sacrificial agent, especially Ce, into catalysts under low temperature might be the most feasible method to improve sulfur resistance. Future studies will focus on dose of Ce and anti-toxicity mechanism.

5. Conclusions

In this study, harms of NO_x are introduced and a statistics on NO_x emission in China in recent years is made. Subsequently, controlling technologies and generation mechanism of NO_x are described. At present, SCR is a mature technology. Several catalysts for SCR reaction are analyzed and the promising application prospects of molecular sieve as a supported catalyst are recognized. Based on analysis of the MnO₂ structure, we believe that analysis of α -MnO₂ surface structure is the only that has to be done at present. Attentions shall be paid to disclose the catalysis principle and active sites and why potassium ion can stabilize pores. By analyzing catalytic performance of MnO₂, this study finds two disadvantages of MnO₂ catalyst, which are excessive strong oxidization and poor sulfur resistance. Finally, we suggested to increasing acid sites and introducing in sacrificial agent to improve the sulfur resistance.

Moreover, future research keys are proposed, which are the dosage of Ce and anti-toxicity mechanism.

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