

Advances in Selective Catalytic Reduction Denitrification Catalysts

Junkai Li

Department of chemical engineering and technology, Guangdong University of Technology,
Guangzhou, China

3121009558@mail2.gdut.edu.cn

Abstract. In recent years, significant progress has been made in the research of catalysts for Selective Catalytic Reduction (SCR) denitrification, and the design and synthesis of novel catalysts have improved the efficiency and selectivity of SCR technology in reducing NO_x emissions. In this paper, several commonly used catalytic preparation methods are firstly introduced. Then the denitrification catalysts were classified into two categories, loaded and unloaded catalysts, and analysed in detail. The characteristics of catalysts such as crystal structure, specific surface area and pore structure have an important influence on the SCR performance, while the active sites and the mode of action of the reducing agent also play a decisive role. Improving the composition, structure and preparation process of catalysts is an important means to improve the activity and stability of catalysts. Future directions include in-depth study of the relationship between catalyst structure and performance, exploration of more efficient catalyst design and preparation methods, enhanced research on the reaction mechanism of SCR denitrification, and commitment to the study of green and sustainable SCR denitrification catalysts.

Keywords: Denitrification catalysts, NO_x, SCR.

1. Introduction

Nitrogen oxides (NO_x) are an important component of acid rain, haze, etc. Large amounts of NO_x emissions can even cause a lot of problems such as photochemical smog and ozone hole, which cause damage to the ecological environment and even have a serious impact on human life and the growth of plants and animals [1]. Therefore, controlling NO_x emissions is an urgent task to solve the current environmental problems. Common NO_x removal technologies include: solid adsorption, plasma, wet nitrogen removal, catalytic decomposition, selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR) [2], of which ammonia selective catalytic reduction (NH₃-SCR) has been widely used due to its high efficiency, low cost and good stability.

SCR is a technology used to reduce emissions of NO_x from gases. The technology uses a catalyst to chemically react urea or ammonia with NO_x in flue gas at a certain temperature to produce harmless nitrogen and water vapour. SCR technology is commonly used in facilities such as diesel engines, coal-fired power plants, boilers, and other facilities to satisfy environmental regulations for NO_x emissions. SCR technology is widely used for its high efficiency in emission reduction and flexibility, and plays an important role in the industrial and transportation sectors. This paper reviews the common preparation methods of SCR catalysts and the research progress of loaded SCR denitrification catalysts versus unloaded SCR denitrification catalysts in recent years.

2. SCR catalyst preparation method

Currently, the main preparation methods for SCR denitrification catalysts include impregnation, hydrothermal method, sol-gel method, in-situ growth method, ion-exchange method, co-mixing method, and co-precipitation method, etc. Among them, impregnation, co-precipitation, and sol-gel method are commonly used in the preparation of low-temperature denitrification catalysts, while hydrothermal method is commonly used in the preparation of denitrification catalysts with homogeneous particles.

The preparation method has a large influence on the activity of the catalyst. Xu et al. [3] compared the activity of Mn-Ce/TiO₂ catalysts prepared by the sol-gel method, the impregnation method, and the combination of the two methods. It was found that the Mn-Ce/TiO₂ prepared by the sol-gel method had a larger specific surface area than the other two preparation methods, had the best denitrification activity, and the conversion of NO at 240°C was more than 90%. Chen et al. [4] prepared Mn-Co-Fe/TiO₂ catalysts by a novel co-precipitation method with NO conversion close to 98% at 500°C. Li et al. [5] prepared Mn/DE-HAL catalysts by impregnation and in situ growth methods, respectively. It was found that the active components of the Mn/DE-HAL catalyst prepared using the impregnation method were distributed on the surface and inside of the carrier, while the active components inside the carrier were not easy to participate in the SCR reaction because of the mass transfer resistance, and the catalytic activity of the catalyst was poor at low temperatures.

3. SCR catalyst classification

3.1. Loaded catalysts

3.1.1 SCR catalysts with TiO₂ as carrier

TiO₂ as a new type of material carrier that has attracted much attention, is the most widely used SCR denitrification catalyst carrier in the industrial field, accounting for 80%-90% of the total weight of denitrification catalysts. The catalytic effect of TiO₂ mainly comes from the transition metal nature of Ti, and the electronic structure of its outer layer is 3d² 4s², which will have a direct effect with the reactants or have an indirect effect on the reaction under different reaction conditions. Orbital hybridisation with s or p orbitals, the directionality of each orbital is weaker than that of s-p hybridised orbitals, so the bonding energy of Ti and ligand is weaker, and catalysis tends to be more ionic [6].

At present, the applications of TiO₂ carrier catalysts mainly include pure TiO₂ carrier denitrification catalysts, M (V, W, Mo, etc.)-TiO₂ composite carrier denitrification catalysts, Ce-TiO₂ and other rare-earth metal element carrier denitrification catalysts. Song et al. [7] discussed the advantages and disadvantages of nano TiO₂ solid catalysts through the study of TiO₂ solid phase carriers and loading methods, and pointed out that it can be combined with filtration or purification equipment, and has a wide range of prospects for application in the field of water treatment and air purification. Xu et al. [8] impregnated W onto TiO₂ to obtain a catalyst with a large specific surface area and a high catalytic efficiency, and WO₃ can play the role of co-catalyst as well as increase the Bronsted acidity of the catalyst to improve the activity of the catalyst. Jin et al. [9] used Mn-Ce composite oxides as the active component of the catalyst, loaded on TiO₂, to obtain excellent low-temperature SCR catalysts, with a NO removal rate of 80% at 120°C.

3.1.2 SCR catalysts with Al₂O₃ as carrier

As a non-metallic oxidant, Al₂O₃ has better anti-sulphation properties, and the production cost of Al₂O₃ is relatively low compared with some high-end carriers, making it suitable for large-scale applications. Al₂O₃ has a large specific surface area, which is conducive to the dispersion of active components and the adsorption of reactive substances.

Liu et al. [10] investigated the effects of preparation parameters, temperature, and airspeed on denitrification activity by coating γ -Al₂O₃ membrane impregnation method with active components CuO and Na₂O, respectively. It was found that due to the alkali metal additives promote the oxidation of NH₃ and inhibit the denitrification activity, the suitable operating temperature of this catalyst is 400°C, the suitable operating airspeed is 2300 h⁻¹ below, and the NO conversion rate is 85%, while for the granular CuO/Al₂O₃ under the same test conditions, the NO conversion rate is above 90%. Guo et al. [11] prepared Al₂O₃ carrier with large specific surface area by gel method, and then formulated CeO₂-MnO_x/Al₂O₃ catalyst loaded with MnO_x and CeO₂ components by equal volume impregnation method, and finally proved that 550°C is the optimal roasting temperature of the catalyst, and the maximum activity of the catalyst can be up to 98% at this temperature, and 4% CeO₂-7% MnO_x/Al₂O₃ is the best catalytic activity ratio, and the optimum operating temperature is 260°C.

3.1.3 SCR catalysts based on molecular sieves

Loaded molecular sieve catalysts are active component catalysts (e.g. vanadium, molybdenum, etc.) loaded on the surface of molecular sieves, which provide a good distribution of active centres and reaction channels through their highly ordered pore structure and large specific surface area, thus facilitating denitrification reactions. The molecular sieve-based catalysts loaded by transition metal ions (Cu, Fe, etc.) were found to have high thermal stability, and their activity windows (200~400°C) were suitable for diesel vehicle exhaust treatment. In particular, molecular sieve-based catalysts with small pore sizes are widely studied for diesel vehicle exhaust gas post-treatment systems at this stage because they exhibit higher NO_x decomposition efficiency and N₂ selectivity during denitrification, are non-toxic and harmless in themselves, and have higher resistance to water and sulfur poisoning, which meets the National VI emission standards for motor vehicles [12]. Lu et al. [13] prepared Cu-SAPO-34 catalyst by in situ hydrothermal method using morpholine as template agent. The ability of molecular sieve catalysts to catalyze the reduction of NO was evaluated on a catalyst evaluation device, and it was found that the denitrification activity of Cu-SAPO-34 was lower at temperatures lower than 100°C. The denitrification activity of Cu-SAPO-34 was reached a maximum of 86% at 250°C. The denitrification activity of Cu-SAPO-34 catalyst started to decrease when the temperature was higher than 300°C. Zhang et al. [14] compared the denitrification properties of different copper-based molecular sieves Cu-ZSM-5, Cu-SSZ-13 and Cu-SAPO-34, and found that Cu-SSZ-13 and Cu-SAPO-34 molecular sieves with CHA-type of small pore size were found to have higher SCR activity, carbon build-up resistance and hydrothermal stability than that of Cu-ZSM-5.

3.1.4 Other carrier SCR catalysts

In addition to the several widely used loaded denitrification catalysts mentioned above, common carriers include activated carbon, zirconia, molybdenum, silicon and so on. Fan et al. [15] prepared loaded catalysts using La-Mn chalcocite oxide as the active component and biochar as the carrier, and concluded that at an airspeed of 16,000 h⁻¹, [NH₃]=[NO]=670 mg/m³, [O₂]=5% (v/v), and a total gas volume of 800ml/min, the loaded catalysts with a range of 100-250 °C 10% NO conversion of LMO/BCNA was greater than 80% with N₂ selectivity greater than 90%, and the maximum NO conversion was 95.6% at 225°C, corresponding to N₂ selectivity of 95.4%. Zhang et al. [16] prepared TiO₂-ZrO₂ solid solutions with a molar ratio of 1:1 by co-precipitation method and impregnated 1% V₂O₅ with different mass ratios step by step, and finally obtained a series of 1% V₂O₅-x%WO₃/TiO₂-ZrO₂, and found that the effect of ZrO₂ on the specific surface area of the catalyst was relatively obvious, and the ZrO₂ was conducive to the dispersed loading of active components. Shen et al. [17] prepared Ti-Al-Si-O_x denitrification catalyst carriers by extrusion moulding method, and optimized the distribution ratio of carrier groups by orthogonal design, and found that when the molar ratio of Ti/Al/Si elements was 1:0.2:0.1, the activity and axial crushing strength of its carrier for SCR NO removal were the best matched. Under the conditions of airspeed of 7200h⁻¹, and 450~550°C, the NO removal efficiency of the carrier was >80%, and the maximum NO removal efficiency reached 85.8% at 494°C.

3.2. Unloaded catalysts

3.2.1 Mn-based metal oxide SCR catalysts

The valence electron configuration of Mn is 3d⁵ 4s², the electrons in the d orbitals of different valence states of Mn in MnO_x are in a half-filled state, (e.g., 3d⁵ for 2-valent Mn, 3d³ for 4-valent Mn) the electrons in the d orbitals are easy to be migrated to NH₃ and O₂, so MnO_x is able to provide free electrons when it is used as an active component. The stronger the ability of free electron migration, the better the redox performance. Therefore, Mn oxide catalysts possess good low-temperature denitrification performance and play an important role in the reaction of selective catalytic reduction of NO_x by NH₃ [18]. Chen et al. [19] used the rheological phase method to prepare unloaded MnO_x and tested its low temperature activity and water resistance. The unloaded MnO_x was found to have excellent NH₃-SCR activity at low temperatures, with a NO_x conversion of 60% at 50°C and nearly

100% at 80°C. The NO oxidation process on the MnO_x catalyst was inhibited when water vapour was present. Xu et al. [20] obtained β-MnO₂, K-α-MnO₂ and H-α-MnO₂ by hydrothermal reaction of MnSO₄ with (NH₄)₂S₂O₈, KMnO₄, and reflux reaction and decomposition reaction of sufficient amount of (NH₄)₂S₂O₈, respectively. The experimental results showed that H-α-MnO₂ and K-α-MnO₂ both had better low-temperature NO_x removal rate, and with the increase of temperature, the NO_x removal rate increased and reaches the highest value close to 100% at 150°C. The low-temperature NO_x removal effect of β-MnO₂, on the other hand, was quite different from that of K-α-MnO₂ and H-α-MnO₂, and the NO_x removal rate was only 70% between 200°C and 300°C. The results showed that the low-temperature NO_x removal rate of β-MnO was only 70%.

In order to further enhance the denitrification performance of Mn oxide catalysts, additives are usually added to the Mn oxide catalysts. Yan et al. [21] doped Ti and Sn in MnO_x-CeO₂ catalysts, and found that the doping of Ti and Sn significantly improved the denitrification rate of the catalysts. The denitrification rate of the catalyst reached more than 90% when the gas air velocity was 60,000 m L/(g·h) at temperatures ranging from 175°C to 300°C. The catalysts were also found to have a higher denitrification rate when the gas air velocity was 60,000 m L/(g·h). More in-depth studies showed that the doping of Ti or Sn increased the surface area of the catalyst, enhanced the oxygen storage capacity, increased the surface acidity, and constituted a redox cycle reaction, which enhanced the denitrification performance of the original catalyst.

3.2.2 Other metal oxide SCR catalysts

In addition to Mn oxide catalysts, vanadium oxide, tungsten oxide, iron oxide, and zirconium oxide are commonly used as SCR denitrification catalysts. In order to investigate the reasons for the good denitrification activity of tungsten-cerium-zirconia catalysts, Xu et al. [22] prepared single-component CeO₂, WO₃, and ZrO₂ catalysts, two-component 50Ce-50Zr, 50W-50Ce, 50W-50Zr catalysts, and three-component 50W-25Ce-25Zr catalysts by the co-precipitation method, among which the three-component tungsten-cerium-zirconia catalysts had the optimal denitrification activity, and concluded that the reason for its better denitrification performance could be attributed to the fact that it had the best denitrification activity. The three-component tungsten-cerium-zirconium catalyst has the optimal denitrification activity, and it was concluded that its better denitrification performance can be attributed to the good dispersion of W on the catalyst surface, higher surface oxygen ratio, and more surface acid sites. Xu et al. [23] optimised a monolithic Fe₂O₃ catalyst by co-precipitation method in the presence of Co, which greatly enhanced the reaction performance of a single Fe₂O₃ catalyst. Subsequently, the catalyst performances of FeCo alone, Ti only or Mn only with simultaneous addition of MnTi were compared, and it was found that only when MnTi was added at the same time, the performance of the catalysts was enhanced over the whole reaction temperature interval, indicating the existence of synergistic effect between Mn and Ti in Fe₂O₃ catalysts.

4. Summary

Currently, in the research of SCR denitrification catalysts, some significant progress has been made, and the design and synthesis of new catalysts make the SCR technology more efficient and selective in the reduction of NO_x emissions, and the characteristics of the catalysts, such as the crystal structure, the specific surface area, and the pore structure, have an great influence on the SCR performance. In addition, the active sites on the catalyst surface and the mode of action of the reducing agent also play a decisive role in the SCR reaction. These findings provide guidance for further optimisation of catalyst structure and performance. By improving the composition, structure and preparation process of the catalysts, the activity and stability of the catalysts have been continuously improved to show better performance in practical industrial applications. In addition, some new types of SCR denitrification catalysts, such as composite catalysts based on transition metal oxides and non-precious metal catalysts, have gradually attracted the attention of researchers, providing new ideas and possibilities for future development. Various composite catalysts based on metal oxides

and transition metals have also been proved to have good catalytic performance, which provides a broad space for the development of SCR denitrification technology.

For the future development direction of SCR denitrification catalysts, I believe that we should continue to study in depth the relationship between catalyst structure and performance, and explore more efficient catalyst design and preparation methods. At the same time, research on the reaction mechanism of SCR denitrification should be strengthened in order to better understand and optimise the performance of the catalyst. In addition, with the increasing requirements of environmental protection, the study of green and sustainable SCR denitrification catalysts will also become an important direction in the future.

References

- [1] Denise Mauzerall, Babar Sultan, Namsoug Kim, et al. NO_x emissions from large point sources: variability in ozone production, resulting health damages and economic costs. *Atmospheric Environment*, 2005, 39 (16): 2851-2866.
- [2] Song Liyun, He Hong, Li Jian, et al. Progress in cerium based catalyst for selective catalytic reduction of NO_x by NH₃. *Journal of the Chinese Society of Rare Earths*, 2017, 35 (1): 69-82.
- [3] Xu Ying, Yan Dongjie, Huang Xuemin, et al. Influence of preparation method on the low-temperature selective catalytic reduction activity of Mn-Ce/TiO₂ catalyst. *Journal of Environmental Engineering*, 2015, 9 (02): 862-866.
- [4] Chen Huanzhang, Li Hong, Li Hua. Preparation of Mn-Co-Fe/TiO₂ catalyst and its low-temperature denitrification performance. *Chemical Engineering*, 2016, 44 (08): 6-10.
- [5] Li Jian, Shi Liming, Lyu Shuangshuang, et al. Preparation of low-temperature SCR denitrification catalysts by manganese oxide-loaded diatomite-erolite porous ceramics. *Environmental Chemistry*, 2023, 42 (10) 3568-3578.
- [6] Xu Jianwen, Wang Jiyuan, Chen Shaohui, et al. Research progress of titanium dioxide in catalysis. *Modern Chemical Industry*, 2011, 31 (05): 21-24+26.
- [7] Liu Minghao, Song Wulin, Lu Zhao, et al. Progress in the study of solid-phase carriers of titanium dioxide nanoparticles. *Materials Herald*, 2021, 35 (09): 9108-9114.
- [8] Xu Hong, Liao Xin, Qin Jianfeng, et al. Study on the selection of tungsten salt precursor in titanium tungsten powder for denitrification catalyst. *Inorganic salt industry*, 2014, 46 (05): 73-76.
- [9] Jin Ruiben. Preparation, reaction mechanism and sulphur resistance of loaded Mn-Ce series low-temperature SCR denitrification catalyst. *Zhejiang University*, 2010.
- [10] Liu Qingya, Liu Zhenyu. Honeycomb cordierite-based CuO/Al₂O₃ catalysts for simultaneous flue gas desulphurisation and denitrification. *Journal of Fuel Chemistry*, 2004, (03): 257-262.
- [11] Guo J. Study on the performance and mechanism of denitrification by CeO₂ modified MnO_x/Al₂O₃ in low temperature SCR method. *Hunan University*, 2011.
- [12] Liu N. Preparation of monolithic Cu-based ERI-type molecular sieve catalyst and its NH₃-SCR performance. *Jiangxi Normal University*, 2023. DOI: 10.27178/d.cnki.gjxsu.2023.001304.
- [13] Lu Yajing, Gou Liyuan, Peng Yu. Preparation of Cu-based SAPO-34 catalyst and its denitrification performance. *Functional Materials*, 2023, 54 (07): 7165-7170.
- [14] Zhang Ranran, Li Yonghong. Research progress of Cu-based molecular sieve NH₃-SCR denitrification catalyst. *Modern Chemical Industry*, 2015, 35 (08): 67-71. DOI: 10.16606/j.cnki.issn0253-4320.2015.08.002.
- [15] Fan Xiaoxiong, Hao Lifang, Fan TuiGang, et al. Study on catalytic denitrification performance of LaMnO₃/biochar catalyst for low-temperature NH₃-SCR. *Journal of Chemical Engineering*, 2023, 74 (09): 3821-3830.
- [16] Zhang Yaping, Wang Longfei, Li Juan, et al. Promotion of ZrO₂ and WO₃ in V₂O₅-WO₃/TiO₂-ZrO₂ denitrification catalysts: catalytic properties, morphology, and reaction mechanism. *Journal of Catalysis*, 2016, 37 (11): 1918-1930.

- [17] Yuesong Shen, Yuhao Zong, Guorong Sui, et al. Component optimisation and performance study of Ti-Al-Si-O_x denitrification catalyst carrier. *Journal of Inorganic Materials*, 2015, 30 (05): 542-548.
- [18] Liu Ting, Wang Tingchun, Wu Ruiqing, et al. Research progress of low temperature NH₃-SCR denitrification catalyst. *Journal of Safety and Environment*, 2012, 12 (06): 36-42.
- [19] Chen Jianjun. Development of manganese-based catalyst and its mechanism of low temperature selective catalytic reduction of NO_x. Tsinghua University, 2007.
- [20] Yujia Xu. Optimisation of MnO_x/TiO₂ low temperature denitrification catalyst and its performance analysis. *China Electric Power*, 2013, 46 (07): 138-142.
- [21] Yan Xiong, Tang Changjin, Yao Xiaojian, et al. Effect of metal ions doping (M=Ti⁴⁺, Sn⁴⁺) on the catalytic performance of MnO_x-CeO₂ catalyst for low temperature selective catalytic reduction of NO with NH₃. *Applied Catalysis A: General*, 2015, 495: 206-216.
- [22] Xu Jia, Zhang Xinjian, Qi Guoqin, et al. Tungsten-cerium-zirconium composite metal oxide catalysts for medium and high temperature NH₃-SCR reaction. *Journal of Nanjing University of Technology (Natural Science Edition)*, 2022, 44 (04): 395-404.
- [23] Xu Peng. Development of iron oxide-based catalysts and study of NH₃-SCR reaction performance. Sichuan University, 2021. DOI: 10.27342/d.cnki.gscdu.2021.004605.