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Improvement of High-efficiency Green Catalysts for Flue Gas Denitrification

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Abstract Based on the basic principle and mechanism of flue gas denitrification, the commonly used catalysts for flue gas denitrification were introduced firstly, and then the catalytic performance, stability and reaction mechanism of catalysts in the market were analyzed. Different types of catalysts were studied to look for green catalysts with high activity, sulfur resistance, water vapor resistance and other advantages. The mechanism of denitration reaction of green catalysts was discussed, and the laws of formation, propagation and consumption of active species in the reaction process were revealed to provide theoretical basis for optimizing catalyst design and improving reaction conditions. Then the research status and problems of new catalysts for flue gas denitrification were described. Finally, the future development direction of green catalysts for flue gas denitration was discussed to improve the performance and stability of catalysts and meet the performance requirements of denitration catalysts in different industries.

Key words Flue gas denitration; Green catalyst; Denitration catalyst; Activity; Selective catalytic reduction; Catalyst activation

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Green denitrification catalysts can effectively decrease the content of nitrogen oxides in flue gas, reduce the pollution of atmospheric environment, improve air quality and protect the ecological environment. Moreover, its research and application can help thermal power plants and other enterprises to realize the standardized discharge of NO_x, reduce energy consumption and greenhouse gas emissions, and be beneficial to China to achieve the reduction of carbon emission. It can also promote technological innovation in related industries, enhance industrial competitiveness, and provide technical support for China's flue gas denitration technology to occupy a place in the international market. Green denitrification catalysts have high activity, stability and regeneration performance, which can reduce the frequency of catalyst replacement, save resource consumption, and facilitate the recycling of resources. Besides, it can achieve efficient, economic and environmentally friendly denitration effect, and reduce the operating cost of thermal power plants and other enterprises. Green and sustainable catalyst materials are used to reduce resource consumption and secondary pollution. Meanwhile, it can improve the research level and application effect of flue gas denitrification technology, and promote the technological innovation of related industries.

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1 Principle and mechanism of flue gas denitration

1.1 Generation and emission sources of nitrification (NO_x)

Nitrous oxide (NO_x) is a class of compounds containing nitrogen oxides (NO_x), mainly including nitric oxide (NO) and nitrogen dioxide (NO_2). Their generation and emission sources are mainly large amounts of NO_x emissions during industrial production. In the fuel combustion process of motor vehicles such as cars and trucks, a certain amount of nitrogen oxides will be produced. Especially in the case of urban traffic congestion, the amount of NO_x emitted by vehicles is more large. Meanwhile, a certain amount of nitrogen oxides will be produced in the process of fertilizer application and rice growth in agricultural production. Coal-fired power generation is one of the main sources of NO_x emission in China. During coal combustion, nitrogen and nitrogen compounds in fuel will be converted to NO_x. In the process of waste incineration, organic nitrogen compounds are oxidized at a high temperature to produce NO_x. In short, nitrification is generated and discharged from a wide range of sources, involving industry, transportation, agriculture, natural environment and many other aspects. In order to reduce the impact of NO_x on the environment and human health, it is necessary to strengthen pollution control and control measures, improve energy utilization efficiency, and promote clean energy and green transportation.

1.2 Principles and objectives of flue gas denitration Flue gas denitration mainly means reducing the content of nitrogen oxides (NO_x) in flue gas to alleviate the pollution of atmospheric environment. Denitration technology is divided into three categories: thermal, chemical and physical denitration technology. Among them, the more common method is selective catalytic reduction (SCR).

The denitration principle of selective catalytic reduction (SCR) is to reduce nitrogen oxides in flue gas to harmless nitrogen and water under the action of a catalyst. The reaction process is as follows:

NH_3 (liquid ammonia) + NO_x (nitrogen oxide) → N_2 (nitrogen) + H_2O (water)

The goal of flue gas denitrification is to reduce the emission of nitrogen oxides in flue gas, alleviate the pollution of atmospheric environment, and improve air quality[4].

1.3 Action mechanism of catalysts in denitration process Catalysts have a large specific surface area and porous structure, and can effectively adsorb nitrogen oxide molecules in flue gas, so it can be used in the denitration process. The nitrogen oxide molecules adsorbed on the surface of a catalyst react with reducing agents (such as NH_3) to promote denitration reaction. The active components in catalysts have higher activity under specific temperature and atmosphere, and can accelerate the reaction between nitrogen oxides and reducing agents, and improve denitrification efficiency. Under the action of catalysts, the nitrogen oxides in flue gas (such as NO_x) and reducing agents (such as NH_3) undergo a redox reaction to produce harmless nitrogen and water. Catalysts can provide right reaction conditions to promote the reaction.

2 Flue gas denitrification catalysts commonly used

At present, the catalysts used in SCR process of flue gas denitrification include vanadium and titanium , precious metal, and metal oxide catalysts.

2.1 Vanadium and titanium catalysts Vanadium and titanium catalysts are most widely used in the denitrification of flue gas in power plants. Vanadium catalysts with TiO_2 as the support mainly include V_2O_5/TiO_2, $V_2O_5-WO_3/TiO_2$, $V_2O_5-MoO_3-TiO_2$, $V_2O_5-WO_3-MoO_3/TiO_2$, *etc.* As the active carrier, TiO_2 plays a dispersing role, and has a small particle size (usually nanometer scale) and a large specific surface area. It provides sufficient contact area for active components, and can also improve the ability of catalysts to resist SO_2. It is generally made into honeycomb, plate, and corrugated types.

2.2 Precious metal catalysts Precious metal catalysts mainly contain Pt, Pd, Rh, Ag, *etc*[1]. Precious metals are loaded with K^+, Na^+, Ca^{2+} in zeolite in the form of ions onto zeolite or alumina, silicon oxide and zirconia by exchange, so as to make a catalyst. Precious metal catalysts have a high low-temperature catalytic activity, but has a narrow activity window and high production cost, so it is not suitable for large-scale treatment of NO_x from a fixed source. Therefore, it has been gradually replaced by metal oxide catalysts and is currently only used for the removal of NO_x from automobile exhaust at a low temperature[2].

2.3 Metal oxide catalysts Metal oxide catalysts mainly include V_2O_5, WO_3, Fe_2O_3, CuO, CrO_x, MNO_x, MoO_3, NiO, and other metal oxides or their mixtures, usually TiO_2, Al_2O_3, SiO_2 and ZrO_2.

3 Research progress of novel catalysts for flue gas denitrification

3.1 Catalysts based on nanomaterials Catalysts for flue gas denitrification based on nanomaterials are an area of extensive research, aiming at reducing the emission of nitrogen oxides (such as NO_x) in flue gas.

(1) Titanium dioxide (TiO_2) nanomaterials: TiO_2 nanomaterials have a good photocatalytic property. (2) Carbon-based nanomaterials: carbon nanomaterials such as carbon nanotubes. (3) Transition metal oxide nanoparticles: transition metal oxide nanomaterials, such as tungsten oxide (WO_3), titanium oxide (TiO_2), nickel oxide (NiO), *etc.* (4) Other nanomaterials, such as nano silver, nano zirconia, nano cerium oxide, *etc*[3].

3.2 Catalysts based on non-precious metals New flue gas denitrification catalysts should be developed based on non-precious metals to improve their activity, stability and selectivity.

(1) Metal oxide catalysts: metal oxide catalysts such as titanium dioxide (TiO_2), tungsten oxide (WO_3), *etc.* (2) Mixed metal oxide catalysts: By mixing two or more metal oxide materials, the composite catalyst formed can improve the catalytic performance of denitrification, such as CeO_2-WO_3, $TiO_2-V_2O_5$, *etc*[4]. (3) Carbon-based materials: carbon-based materials such as graphene, carbon nanotubes, activated carbon, *etc.* (4) Supported non-precious metal catalysts: non-precious metal catalysts are loaded on a suitable carrier, such as oxide, activated carbon, and nanomaterials[5].

3.3 Catalysts based on nanocomposites The novel flue gas denitrification catalysts based on nanocomposites are usually composed of a variety of nanoscale active components and carrier materials, and have high specific surface area and abundant active sites, thus showing excellent catalytic performance.

(1) Nano-metal oxide composite catalysts: nano-composite catalysts composed of two or more metal oxides, such as Fe_2O_3/MNO_x, CuO/Fe_2O_3 and ZnO/MNO_x. (2) Nano-metal-organic skeleton (MOF) catalysts: nano-composite catalysts based on MOF materials, such as ZnO@ZIF-8, Cu-DOBDC and Fe-ZSM-5, *etc.* (3) Nano-carbon composite catalysts: MNO_x/ graphene, Fe_2O_3/ carbon nanotubes and CuO/ carbon points. (4) Nano-oxide/reducing carrier composite catalysts: TiO_2/SiO_2, Fe_2O_3/Al_2O_3 and CuO/ZrO_2[6].

3.4 Analysis of catalytic activity, selectivity and cost advantages of novel catalysts New catalysts are usually prepared with highly efficient active materials or nanomaterials, and have a larger specific surface area and more active sites, so that the catalytic reaction can be more fully carried out. This means that more nitrification can be converted to nitrogen instead of producing by-products, which improves the efficiency and environmental protection of the denitrification process. Since new catalysts generally have higher activity and selectivity, denitrification reactions can be carried out at lower temperatures and pressures, which reduces equipment operating costs.

4 Research status and problems of catalysts for flue gas denitrification

4.1 Review of research results and application Flue gas denitrification technology is a technical means to effectively control nitrogen oxides for effective treatment. In the reaction process of this method, no by-products are produced, and the structure of the operating device is simple, with high denitration efficiency. Catalysts are the core of the technology, and their performance will affect the speed of the reaction and the change of the structure of the product, directly affecting the denitration effect.

Catalysts for flue gas denitration can be divided into honeycomb, plate and ripple catalysts according to their structure, and heavy metal catalysts, metal oxide catalysts and so on according to their materials[2].

At present, honeycomb catalysts have the highest utilization rate in the commercial market, and their specific surface area and porosity are large, which can make the agent and the carrier fully mixed and fully reacted. The principle of corrugated catalysts is similar to that of honeycomb catalysts, so as to achieve a better flue gas denitrification effect. Metal oxide catalysts have been widely used at home and abroad because of their low price, ultra-multi-pore structure and better catalytic effect.

Presently, the main catalyst used in kerosene-burning power plants uses anatase type titanium dioxide as a composite carrier, and then vanadium oxide is added to the carrier as an active component; tungsten trioxide is used as a cocatalyst. The catalyst not only has the characteristics of a honeycomb catalyst, but also has the excellent characteristics of low price and many micropores of metal oxides[7].

4.2 Problems and challenges in existing research The main problems of catalysts for flue gas denitrification are ash accumulation and blockage, sintering and volatilization of active components, poisoning and mechanical wear of catalysts. These problems will lead to the deactivation of catalysts, which will seriously affect the effect of catalysts on flue gas denitrification[8].

5 Future development direction

Under the background of green development, low-temperature SCR technology is the main denitrification technology at present[9]. The key of low-temperature SCR technology lies in catalyst. Therefore, a future research focus is to further modify catalysts, improve the performance and stability of catalysts, and meet the performance needs of different industries for denitrification catalysts[10].

The research, development and application of new catalysts are also the focus of research on catalysts for flue gas denitrification. At present, the low-temperature denitrification catalysts reported mainly include precious metal, carbon-based and metal oxide catalysts. However, these catalysts are still facing difficulties[11]. The cost of precious metal catalysts is relatively high, and it is easy to generate N_2O due to high catalytic activity, with poor water resistance. The hydrothermal stability and preparation cost of molecular sieve catalysts are high. Modified carbon-based catalysts have good low-temperature denitrification activity, but their life is an important problem restricting their application. If a new type of flue gas denitrification catalysts with good water resistance, high economic efficiency and long service life are developed, the current problems can be solved. The research and development of new green denitrification catalysts with high efficiency and good effect under conditions of wide temperature and complex flue gas has become an important topic in the field of flue gas efficient denitrification[12].

6 Conclusion

The exploration of multi-catalyst combination and process optimization is an important development direction in the future. Presently, each catalyst studied has its own advantages and disadvantages. It is one of the optimal methods to improve the catalytic level by trying to combine multiple catalysts and optimize the process. Multiple catalysts are combined to solve the problems of poor water resistance and low-temperature activity, so that catalysts have a wider application range to solve problems efficiently[13]. By blending with transition metal oxides and rare earth metal elements, as well as the improvement and application of nanomaterials, the process is optimized to improve the performance of catalysts[14].

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