Effect of microwave radiation on pore structure of SCR denitration catalyst

Honghong Shen\(^1\), Qunyin Gu\(^2\), Daoyuan Wen\(^2\), Gang Liu\(^1\)\(^-\)\(^3\), Weijun Gao\(^3\), and Jianxing Ren\(^1\)

\(^1\)Colleg of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai, China
\(^2\)Department of International Environmental Engineering, \=`The University of Kitakyushu, Fukuoka, Japan
\(^3\)Guodian Tongling Power Generation Co.Ltd, Anhui, China
e-mail: hh20180606@126.com

Abstract. Based on the background of SCR denitification technology widely used in pulverized coal utility boilers, the characteristics of denitification catalysts used in industry were studied. Microwave radiation was used to prepare 8Mn-8Fe/Al\(_2\)O\(_3\) denitification catalyst by using microwave as an efficient and fast heating method. The results show that microwave irradiation can make the catalyst heated from inside to outside without temperature gradient, make the molecule oscillate rapidly, change the specific surface area and pore structure of the catalyst, thus improving the catalytic activity of the catalyst.

1. Introduction

Nitrogen oxides (NO\(_X\)) \(^1\)mainly come from flue gas emissions from coal-fired power plants and automobile exhaust emissions. The hazards of nitrogen oxides are mainly manifested in four aspects: Nitrogen oxides entering human respiratory system can cause diseases such as tracheitis, pneumonia, emphysema, etc. Nitrogen oxides and human hemoglobin binding ability is stronger than CO, which makes human body anoxic; Nitrogen oxides are an important factor in acid rain formation. Acidic rain can destroy forest vegetation and pollute water body, and bring incalculable loss to our country; chemical reaction between nitrogen oxides and hydrocarbons under sunlight produces a toxic photochemical smog, which seriously threatens human life; the chain reaction between N\(_2\)O in nitrogen oxides and ozone in stratosphere depletes ozone, resulting in ozone hole in the ozone layer. National "Twelfth Five-Year Plan"\(^2\) put forward the most stringent environmental protection standards. By 2020, the plan will reduce NO\(_X\) emissions by another 10%. The situation of emission reduction is urgent.

Selective Catalytic Reduction SCR\(^3\) is a widely used flue gas denitrification technology at present. Catalyst is the core of SCR denitification. Commercial V\(_2\)O\(_5\) titanium dioxide catalyst has high cost, high reaction window temperature, and its active component, heavy metal vanadium, is an environmental pollutant. Therefore, under increasingly stringent NO\(_X\) emission standards and waste management system, an efficient and environmentally friendly catalyst is developed. Agents have far-reaching significance.
2. Denitrification mechanism

In the SCR reactor, the reactant and the flue gas flow through the gas film on the outer surface of the catalyst, and then diffuse to the outer surface of the catalyst; the reactant then diffuses from the outer surface of the catalyst to the microporous surface of the catalyst wall, and then is adsorbed on the surface of the catalyst; the chemical reaction occurs in the gas phase with the adsorption on the surface of the catalyst, and the products are formed and catalyzed. The surface desorption of the chemical reagent gradually diffuses to the outer surface of the catalyst, and finally diffuses from the outer surface of the catalyst through the gas film to the mainstream gas, which is taken away by the flue gas. The microreaction mechanism is shown in Figure 1. and Figure 2.

At present, SCR denitrification catalysts used in industry are mainly ocatalysts, which have high denitrification efficiency at 250 - 350 ℃ reaction temperature. However, the problems of catalyst poisoning and severe poisoning have also been paid more attention. Jiang Ye[4] et al. put forward that coal-fired flue gas contains a certain concentration and a small amount of water vapor which reacts with escaping and flue gas, which will not only reduce the activity of catalyst, but also block the downstream pipeline. At present, scholars at home and abroad have carried out different levels of research on selective catalytic reduction catalysts. The research on new catalysts mainly focused on iron-based, copper-based and doped new catalysts. Wang Fang[5] et al. found that the activation energy was low and the activity was high. The denitrification efficiency reached more than 90% at 250 ℃. The SCR activity of Cssonova[6] catalyst prepared by precipitation method is directly related to its content at low and medium temperatures. Xu Liting[7] et al. found that the maximum denitrification efficiency of the catalyst was 9.1% at 325 ℃. Lu Huixia[8] et al. found that the specific surface area of siderite doped with rare earth elements was larger, the crystallization of catalyst was improved, the surface acidity was improved, and the denitrification efficiency was obviously improved. After 7 hours of continuous operation, the denitrification efficiency of siderite catalyst was still more than 80%, and its sulfur resistance and persistence were also improved. Sun Jiaxing[9] et al. found that when the optimum formulation of the catalyst was 6%, the maximum denitrification efficiency could reach 80% below 200 ℃ in the study of copper-based catalysts modified by transition metal oxides. Catalyst is the core of SCR flue gas denitrification technology. The development of non-toxic, harmless, durable, sulfur-resistant and low-temperature catalysts is of great significance to reduce the operating cost of SCR denitrification system.

Figure 1. Microreaction Mechanism of SCR Flue Gas Denitrification
3. Experiments

The low temperature supported denitrification catalyst 8Mn-8Fe/Al₂O₃ was prepared by co-impregnation method. The effects of common drying method and microwave drying method on the catalyst were compared. The main chemical reagents used were iron nitrate (NO₃)₃·9H₂O, ammonia (25%) and manganese acetate (CH₃COO)₂·4H₂O. The main experimental equipments are oven, microwave oven, magnetic stirrer, muffle oven, electronic balance, measuring cylinder, beaker and glass rod, PH test paper, etc. The content of metal elements in the impregnation process is calculated by mass fraction.

Common preparation method: 50 mL deionized water is put into beaker with dosage barrel, then a certain amount of iron nitrate and manganese acetate is weighed with electronic balance and put into beaker. A solution containing 8% of Mn and 8% of Fe is prepared. The solution is stirred with glass rod until it is completely dissolved 230-425 mm of Al₂O₃ particles are put into the solution and dripped. The ammonia water was continuously stirred to pH=8-9, then stirred for 0.5 h in 50 ℃ water bath by magnetic stirrer, and kept for 48 h at room temperature. Then it was dried at 120 ℃ in oven for 24 h, then calcined in muffle oven at 450 ℃ for 5 h. The catalyst obtained was O-8Mn-Fe/Al₂O₃.

Microwave preparation method: The operation before the method is the same as that of the ordinary preparation method. After the method is stationary, the microwave oven is used for drying, the drying power is 350 W, the drying time is 15 minutes, and then calcined in a muffle oven at 450 ℃ for 5 hours. The catalyst obtained is M-8Mn-8Fe/Al₂O₃.

4. Result discussion

The specific surface area and pore size of O-8Mn-8Fe/Al₂O₃, M-8Mn-8Fe/Al₂O₃ [10] and two kinds of samples were characterized and analyzed by means of specific surface area and porosity analyzer. The BET formula was used to calculate the specific surface area and pore size of the samples. The results are shown in Table 1. Compared with ordinary drying, the specific surface area of the catalysts increased after microwave drying. Additionally, the average pore volume increased slightly, mainly because microwave heating was carried out both inside and outside at the same time, and the heating speed was faster. Moisture was gasified instantaneously. The pore structure of the catalyst was improved to a certain extent by leaving the catalyst by blasting. The average pore size of the catalyst was 6.03 nm, belonging to the mesoporous range, which made the volume flow rate of the gas flow larger (high space velocity). In this case, the resistance of gas diffusion within the catalyst is small, which can ensure a higher denitrification efficiency.
It can be seen from the pore size distribution in Figure 3 [11], the pore size of samples after microwave drying is mostly distributed in 2-4nm, while the pore size of samples after ordinary drying is mostly distributed in 12NM, that is to say, microwave treatment does not significantly change the pore type of catalyst, but changes the pore size distribution, so that the pore structure of catalyst becomes developed, so as to enhance its adsorption capacity and improve its adsorption capacity. Denitration

![Figure 3 Sample adsorption isotherm](image)

| Sample               | Specific surface area $(m^2 \cdot g^{-1})$ | Mean gap $(cm^3 \cdot g^{-1})$ | Average pore size (nm) |
|----------------------|------------------------------------------|-------------------------------|------------------------|
| General drying       | 185.64                                   | 0.3724                        | 8.02                   |
| Microwave drying     | 248.83                                   | 0.3757                        | 6.03                   |

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The grains on the surface of ordinary dried samples are connected into a large number of particles, and the number of micropores is small. According to bet analysis, the micropores are also small, which will hinder the gas diffusion to the catalyst, and is not conducive to the SCR denitration reaction. However, the samples after microwave drying have a good dispersion and a uniform distribution of grains, which increases the contact area between catalyst and gas, making the gas It is easier to adsorb on the catalyst surface, so as to promote the SCR denitration reaction, and the denitration efficiency is also improved at low temperature, as shown in Table 2 [11]. After microwave drying, the pore structure of the sample is more developed than that of common drying, the agglomeration of catalyst is improved, and its micro performance is improved. This is consistent with bet characterization. Therefore, the
samples dried by microwave have larger specific surface area, more developed pore structure, better particle dispersion, and the denitrification performance is far better than the catalyst dried by ordinary

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