Study on the properties of improved adsorbent of nitrogen oxides

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Abstract. In this paper, sodium bentonite, zeolite and other natural minerals are used to make adsorption materials, and physical and chemical adsorption are combined to improve the adsorption efficiency of NOx. The adsorbents were modified by loading additives with high catalytic capacity for NO. Results showed that the improved adsorbent has high adsorption to NO, making NO easy to be oxidized into NO2 by the loaded metal oxides, thus NOx can be highly adsorbed and purified at room temperature.

1. Introduction
The emission of NOx has brought serious harm to the ecological environment and human life. Environmental problems caused by NOx mainly include: toxic effects on humans; Damages to plants; Corrosion of buildings and production equipment; Forming acid rain and fog; Forming photochemical smog with hydrocarbons. In addition, NOx is an important precursor of fine particulate matter (PM2.5).

In the rare and precious metal smelting industry, enterprises use a large amount of nitric acid in the process of pickling, acid dissolution and leaching, resulting in the concentration of NOx up to tens of thousands of milligrams, with intermittent emission characteristics [1, 2].

At present, the NOx produced in rare and expensive metal smelting workshops is generally treated by alkali absorption method, while the traditional alkali absorption method has very limited adsorption efficiency on NO, resulting in the overall adsorption efficiency of alkali absorption on NOx can only reach about 50%[3]. For intermittent and high-concentration NOx treatment, the feasibility of using this method is not high, while the dry adsorption process with small investment, stable operation and low maintenance cost reflects its advantages.

2. The adsorption method
The acid mist adsorbents developed by BGRIMM have a good effect on the treatment of nitric acid gas. It is composed of activated carbon, basic chemicals, zeolite and other components. Activated carbon enhances the adsorption reaction rate through physical adsorption and promotes the conversion of NO to NO2, increases the adsorption reaction rate, and is eventually absorbed by alkaline substances in the adsorbents. Natural zeolite has the skeleton structure, which will form rich crystal hole and has a strong adsorption ability.

However, in the actual application process, it is found that the traditional adsorbent still has problems such as poor mechanical strength, short service life and low adsorption efficiency for NO.
3. Preparation of new dry adsorbent
In order to solve the problems of low adsorption efficiency of NO, the adsorbent components were optimized, and the adsorbent was modified by loading additives with high catalytic capacity for NO.

The preparation process of adsorbent is briefly introduced as follows:
- **Grind fine**: grind all kinds of raw materials separately first, the granularity of grind fine is 200 mesh;
- **Mixing**: add proper amount of water to mix the raw materials;
- **Extruding**: extrude into strips and extrude many times;
- **Loading**: the metal oxide is loaded on the activated carbon by impregnation method, and the excess water is filtered out by filter paper;
- **Drying**: dry under natural conditions, send to infrared drying oven with the temperature of 110 ℃, then send to muffle furnace with the temperature of 400 ℃ for four hours.

In this experiment, impregnation method was used to prepare the catalyst. The concentration of the solution in the study was calculated by conversion according to the amount of metal oxide needed to be loaded on the activated carbon. Adsorbents of 3% and 5% were prepared for the experimental study.

4. Test adsorbent performance

4.1 Efficiency of traditional adsorbent on NOx
According to the preliminary investigation, the ratio of NO2 to NO in the flue gas of rare and precious metals smelting is about 10:1. In order to promote the conversion efficiency of NO, the aerobic condition is carried out, and NO2: NO: O2=10:1:1 in the gas source. The mixture is then humidified by the humidifying bottle and then adsorbed on the adsorption column. The NO2 concentration at the entrance was controlled at about 2700 mg/m³, and the NO concentration was controlled at about 300 mg/m³, with gas velocity 0.2m/s and humidity 30%.

The adsorption efficiency of traditional adsorbent for NO2 was significantly higher than that for NO. The initial NO adsorption efficiency was 30.5%, and it was about 18.9% 6 hours later. The adsorption efficiency of NO2 was higher, starting at 99.97%, and about 88.64% 6 hours later.

![Adsorption efficiency curve of NOx by traditional adsorbents](image)

4.2 Efficiency of improved adsorbent on NOx
A new type of NOx adsorbent was used, with a load of 5% La oxides. The mixture was humidified in a humidifying bottle and then adsorbed on the adsorption column. NO2 concentration at the entrance was controlled at 2700 mg/m³, NO concentration was controlled at 300 mg/m³, gas velocity was 0.2m/s, and humidity was 30%.

The adsorption efficiency of modified adsorbents for NO2 and NO improved obviously. The initial NO adsorption efficiency was 56%, and it was about 41% 6 hours later. The adsorption efficiency of NO2 was 99.6% and 95.7% 6 hours later.
Fig. 2 Adsorption efficiency curve of NOx by modified adsorbents

The sodium bentonite in the modified adsorbent has porous structure and good physical adsorption performance. At the same time, Na2O in sodium bentonite will generate NaOH when it meets water. Compared with pure Ca(OH)2, it increases the reaction rate of acidic gas and further improves the adsorption effect of NO2. At the same time, the supported metal oxide can be used as a catalyst to accelerate the conversion of NO to NO2, and the conversion efficiency is improved by more than 40%, promoting NO2 to be absorbed by the alkaline substances in the adsorbent, thus greatly improving the overall adsorption efficiency of NOx.

5. Characterization test of adsorbents

In order to accurately analyze the adsorption characteristics of the improved adsorbent, the specific surface area and pore size distribution of adsorbent samples were measured by Quantachrome specific surface analyzer. Results showed that the specific surface area of the improved adsorbent was 36.972m²/g. The pore diameter of adsorbent micropores is mostly between 0.85-5nm, with a wide distribution of pore diameter and a large number of micropores below 1.2nm. According to the "effective surface area" theory, the adsorbent is more conducive to the adsorption of NO and NO2 molecules.

The scanning electron microscope pictures of adsorbent before and after the improvement are shown in figure 3.
6. Continuous improvement
The high price of rare earth metal oxides is not suitable for the preparation of large amount of industrial NOx adsorbents, and appropriate alternative materials should be used. Rare earth separation wastewater treatment neutralization slag is an ideal alternative material.

Rare earth separation wastewater treatment neutralization slag refers to the rare earth oxalic acid wastewater lime neutralization slag produced by the neutralization treatment of rare earth oxalic acid wastewater with lime. Its main ingredients are calcium oxalate, oxalic acid rare earth, rare earth hydroxide, calcium hydroxide, ferric hydroxide and aluminum hydroxide, etc., these elements in the process of calcination can produce a series of chemical reactions, and rare earth separation in the waste water and residue after calcination can contain rare-earth metal oxide as Y$_2$O$_3$, La$_2$O$_3$, CeO$_2$, Pr$_6$O$_{11}$, Nd$_2$O$_3$ and alkaline substances as Ca(OH)$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and MgO. The catalytic oxidation of these rare earth metal oxides can accelerate the conversion of NO to NO$_2$, thus improving the adsorption efficiency of NO$_x$.

Experimental study found that after calcining in 800 ~ 1200 ℃ for 2 ~ 4 hours, the quality of rare earth oxides was 4.5% of the total amount. Content of metal oxides in rare earth neutralization residues was shown in table 1. Therefore, the preparation of NO$_x$ adsorbent from rare earth separation wastewater treatment neutralization slag can be used as a new development direction for the preparation of NO$_x$ adsorbent.

| Rare earth oxide | Y$_2$O$_3$ | La$_2$O$_3$ | CeO$_2$ | Pr$_6$O$_{11}$ | Nd$_2$O$_3$ | Sm$_2$O$_3$ |
|-----------------|------------|-------------|---------|---------------|------------|------------|
| Content %       | 23.9       | 28          | 2.1     | 6.5           | 21.5       | 5.0        |

| Rare earth oxide | Eu$_2$O$_3$ | Gd$_2$O$_3$ | Tb$_2$O$_7$ | Dy$_2$O$_3$ | Ho$_2$O$_3$ | Er$_2$O$_3$ |
|-----------------|------------|-------------|-------------|------------|------------|------------|
| Content %       | 0.8        | 5.0         | 0.65        | 3.5        | 1.5        | 1.5        |

7. Conclusion
Physical adsorption and chemical adsorption were combined to improve the adsorption efficiency of NO$_x$ by improved adsorbents. Results showed that the metal oxide can be used as a catalyst to accelerate the conversion of NO to NO$_2$, and the conversion efficiency is improved by more than 40%, which promotes the absorption of NO$_2$ by the alkaline substances in the adsorbent, thus greatly improving the overall adsorption efficiency of NO$_x$.

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