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Preparation and performance of low temperature SCR catalyst on different Supports

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Abstract. Nitrogen oxides (NO_X) are one of the main sources of pollution causing atmospheric pollution, and one of the main causes of acid rain and acid mist. In this paper, low temperature SCR catalysts were prepared by impregnation method. The preparation process and the denitrification rate are optimized by changing the ratio of manganese nitrate and lanthanum nitrate, calcination temperature, carrier, citric acid and the like. At the same time, the physical properties and structural characterization of the catalyst were carried out by SEM and BET. The results showed that the best support was ZSM-5, the loading amount was 14% manganese nitrate, 7% cerium nitrate, citric acid was 1 g, and the calcination temperature was 500 ° C.

1. Introduction

Nitrogen oxides (NO_X), a primary air pollutant, are important substances causing acid rain, chemical smog and other phenomena, and have a damaging effect on plant life, in which NO and NO_2 even have a toxic effect on animals and humans [1]. Global NO_x emissions are rising continuously every year, and the pollution phenomena related to NO_x pollution, such as particulate matter, ozone and atmospheric grey haze, are becoming increasingly serious. Therefore, it is urgent to treat NO_x.

According to the formation mechanism, the main control technologies of NO_x can be divided into pre-combustion control, in-combustion control and post-combustion control. Pre-combustion control technology refers to the process of removing or converting nitrogenous compounds into harmless substances (such as nitrogen) before the combustion of dyes. The control technology in combustion refers to reducing the generation of NO through reforming the burner's structure and controlling combustion conditions. Post-combustion control technology refers to the transformation and treatment of nitrogen oxides in flue gas. The post - combustion technology can be divided into wet flue gas out - of - production and dry flue gas out - production. Selective Catalytic Reduction method (Selective Catalytic Reduction, SCR), because of its mature technology, high denitrification efficiency, simple operation and relatively high cost performance advantages, has become the mainstream of the coal-fired power plant is out of stock at home and abroad technology. Vanadium catalyst such as V_2O_5/TiO_2, V_2O_5-WO_3/TiO_2 is widely used catalyst, its working temperature is above 300 ℃, the temperature is below

300 ℃, the catalytic activity is low [2-6]. Therefore, the hot spot of interest has become a study of SCR technology suitable for the low temperature at the end of the treatment system.

2. The experimental process

With different carrier (ZSM - 5 zeolite, 4 A molecular sieves, gamma Al_2O_3, butyl titanate, Mt - CA), different ratio of cerium nitrate, different calcination temperature (300 ~ 600 ℃), the preparation of SCR catalysts. The denitrification experiment was then performed on the sample to obtain NOx data and the denitrification rate was calculated according to formula (1).

$$NOx_{conversion}\% = \frac{[NOx]_{in} - [NOx]_{out}}{[NOx]_{in}} \times 100\% \qquad (1)$$

Where: $[NO_x] = [NO] + [NO_2]$, the subscripts in and out represent the inlet and outlet concentrations, respectively.

3. Experimental results and discussion

3.1. Determination of optimal loading capacity of manganese nitrate and chromium nitrate

Proper addition of raw materials plays a crucial role in the cost of products. Excessive raw materials will lead to the incomplete use of raw materials, substandard product quality, and insufficient raw materials will waste energy consumption of the entire process. Based on the principle of single variable, the loading capacity of $Mn(NO_3)_2$ and $Ce(NO_3)_3$ was changed to determine the optimal material ratio. The data obtained from the experiment are shown in table 1.

Table 1. Influence of different loads of manganese and cerium on denitrification

Mn load	Ce load	denitrification Rate /%					
		140°C	160°C	180°C	200°C	220°C	240°C
10%	5%	1.91	11.68	17.92	38.38	89.42	94.34
12%	6%	3.47	23.54	35.88	51.19	90.48	99.26
14%	7%	37.16	53.29	65.23	88.53	99.04	99.40
16%	8%	47.88	49.90	62.01	75.86	96.16	95.96
18%	9%	44.88	46.35	59.29	74.56	96.99	98.54

The results show that the denitrification of catalyst is different with the difference of loading capacity of manganese and cerium. denitrification was the lowest when the manganese load was 10%, and the denitrification increased with the increase of the load, and the denitrification was the best when the manganese load was 14%.   When the load exceeds 14%, the denitrification rate decreases as the load increases. So the optimal loading is 14% manganese and 7% cerium.

3.2. Determination of the best carrier

The influence of different Supports on denitrification is shown in figure 1. It can be seen from figure 1 that the activity of the catalyst is different under different loading systems. Overall, ZSM-5 molecular sieve > Mt-CA > butyl titanate > Al_2O_3 > 4A molecular sieve. With the increase of reaction temperature, the activity of each catalyst increased and denitrification increased. The activity of Mt-CA, butyl titanate, 4A zeolite and Al_2O_3 catalysts did not differ significantly at different temperatures, and the activity of ZSM-5 was significantly higher than that of the first four zeolites.
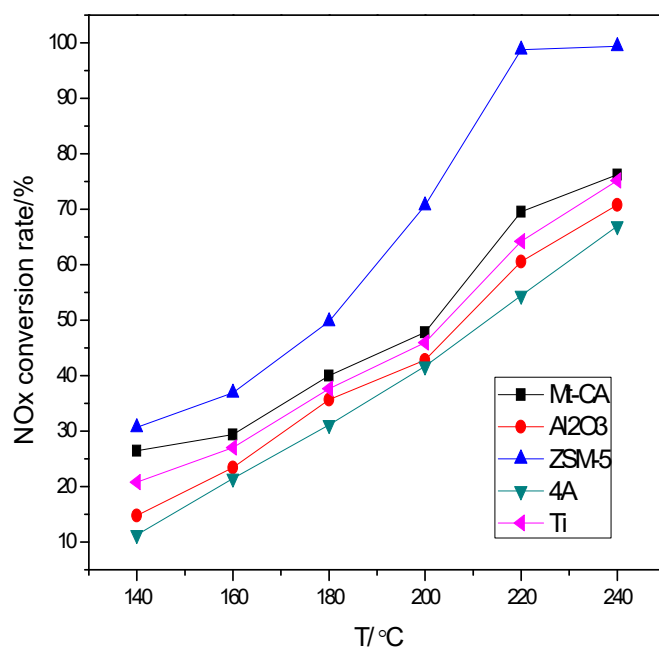
Figure 1. The influence of different carrier for denitrification rate chart

3.2.1. SEM characterization of different Supports. It can be seen from figure 2 that the ZSM-5 molecular sieve particles are uniformly distributed with small particle size, while the 4A *molecular* sieve is unevenly distributed with large particles. The ZSM-5 skeleton has large specific surface area and abundant mesoporous, which reduces the possibility of carbon deposition in the catalytic reaction of macromolecules. Therefore, ZSM-5 molecular sieve is the best support.
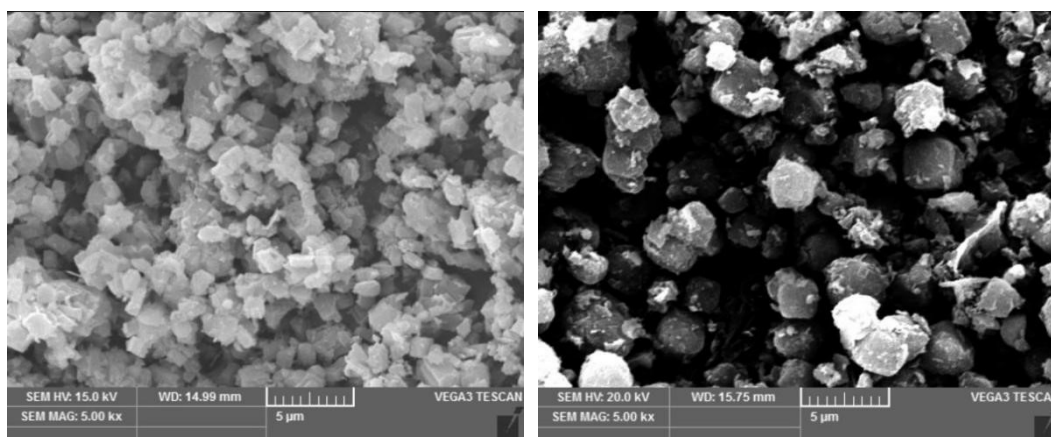

ZSM-5 molecular sieve   4A molecular sieve

Figure 2. SEM images of different supported catalysts

3.3. Determination of the optimum calcination temperature.

3.3.1. Effect of Different Calcination Temperatures on denitrification Rate. It can be seen from Figure. 3 that the catalyst denitrification rate is the highest at a calcination *temperature* of 500 ° C. The other four denitrification rates: 450° C > 400° C > 300° C > 600° C.
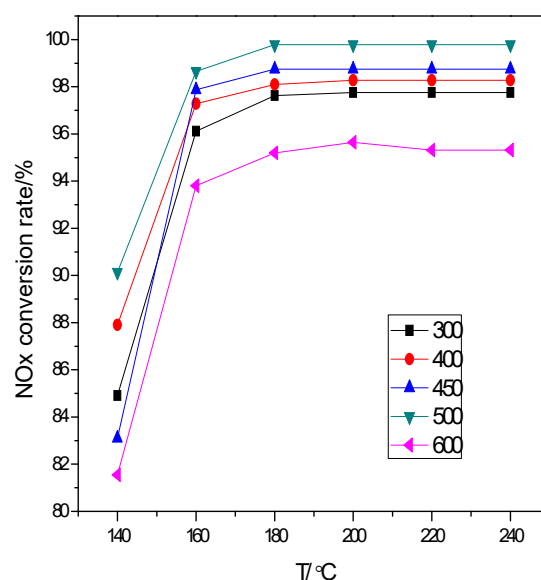
**Figure 3.** Effect of calcination temperatures on denitrification rate

3.3.2. BET characterization at different calcination temperatures. It can be seen from the comparison of Table 2 that, below 500 ° C, as the calcination temperature increases, the specific surface area of the catalyst increases, the average pore volume increases, and the average pore diameter decreases. At 600 ° C, the specific surface area is the smallest, the average pore volume is the smallest, and the average pore diameter is the largest. The increase of the specific surface area increases the contact area of the catalyst with the reaction gas, increases the pore volume, relatively reduces the internal diffusion resistance of the reaction gas during the catalytic reaction, and increases the macroscopic reaction rate. Therefore, the optimum calcination temperature is 500 ° C.

Table 2. Surface area and pore characterization of catalyst

Calcination temperature	Specific surface area/$m^2 \cdot g^{-1}$	Average pore volume/$cm^3 \cdot g^{-1}$	Average aperture/nm
300°C	28.7	0.055	32.0
400°C	30.2	0.085	30.8
450°C	36.8	0.137	19.3
500°C	56.8	0.169	10.8
600°C	25.6	0.026	50.5

3.4. Study on the complexation of citric acid

The effect of the out-of-stock effect of adding different amounts of citric acid is shown in Figure 4. As can be seen from Figure 4, the denitrification rate of citric acid at a temperature of 200 ° C or higher can reach 100%, and even if the reaction temperature is at a low temperature of 140 ° C to 200 ° C, most of them are higher than 80%. As the addition of citric acid increases, the rate of denitrification decreases. Therefore, the optimum amount of citric acid added is 1 g.
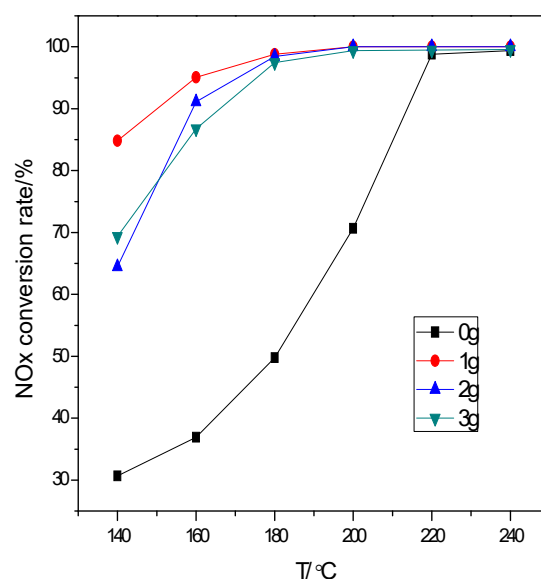
Figure 4. Effect of different amounts of citric acid on denitrification rate

4. Conclusion

In this paper, the low-temperature SCR performance of NH_3-SCR catalyst was comprehensively evaluated, and the low-temperature SCR performance of catalyst was investigated under various reaction conditions by simulating flue gas. The following conclusions can be drawn from the experiment:

(1) For loading the inquiry, the optimum loading was 14% of manganese, cerium 7%, then denitrification efficiency is optimal.

(2) When manganese nitrate or cerium nitrate is the main active material, the optimal carrier is ZSM-5, and the denitrification rate of the catalyst can be up to 99.39%.

(3) When the calcination temperature is 500 ° C, the catalyst denitrification rate is the best, reaching 98.78%.

(4) The addition of citric acid can improve the catalytic effect of the catalyst. the addition amount is 1g.

The above results are consistent with SEM, BET, etc. on the physical properties and structural characterization and results of the catalyst.

Acknowledgments

References

[1]   Kouravand S, Kermani A M. Clean power production by simultaneous reduction of NOx and SOx contaminants using Mazut Nano-Emulsion and wet flue gas desulfurization [J]. Journal of Cleaner Production, 2018, 201: 229-235.

[2]   Chen L, Weng D, Wang J, et al. Low-temperature activity and mechanism of WO_3-modified CeO_2-TiO_2 catalyst under NH3-NO/NO_2 SCR conditions [J]. Chinese Journal of Catalysis, 2018, 39(11): 1804-1813.

[3]   Liqiang Chen, Fulong Yuan, Zhibin Li, et al. Synergistic effect between the redox property and acidity on enhancing the low temperature NH_3-SCR activity for NOx removal over the $Co_{0.2}Ce_xMn_{0.8-x}TiO_{(x=0-0.40)}$ oxides catalysts [J]. Chemical Engineering Journal, 2018, 354: 393-406.

[4]   Yao X, Zhao R, Chen L, et al. Selective catalytic reduction of NOx, by NH_3, over CeO_2, supported on TiO_2 : Comparison of anatase, brookite, and rutile [J]. Applied Catalysis B Environmental, 2017, 208:82-93.

[5]   Guofu Liu,Wenyun Bao,Wei Zhang, et al. The influence of low-temperature hydration methods on the stability of Cu-SAPO-34 SCR catalyst [J]. Journal of the Energy Institute, 2018, 354:85-92.

[6]   Hong H E, Weng D, Xin-Yun Z I. Diesel Emission Control Technologies: A Review [J]. Environmental Science, 2007, 28(6):1169-1177.