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Experimental Study on the Catalytic Reduction of NO_X by Fe and Ce During the Coke Combustion Process

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Abstract. NO_X emissions during the combustion of coal would cause serious pollution to the atmosphere. It is particularly important to reduce NO_X pollution during the combustion process by replacing loose coal with clean coke. The use of clean coke for civil is one of the main ways to reduce NO_X emissions, which is mainly formed by the mixed dry distillation of metal additives and coal. The coke samples with different proportions of metal additives were prepared by physical mixing method, and the NO_X emission law of clean coke at different temperatures was studied in a high-temperature tube furnace reactor. The results show that the addition of Fe alone has a significant effect on the control of NO_X emissions, and the co-doping with Ce can further promote the reduction of NO_X, so as to achieve the final low emission of NO_X. While the reaction temperature is 1000 ℃ and the addition ratio is 2:1, the NO_X reduction rate is 73%. It has important practical value and scientific significance for the clean utilization of coal and the treatment of NO_X in the atmosphere.

1 Introduction

As a primary energy source, direct combustion of coal is the main way of utilization. However, the contribution of coal combustion to the emission of NO_X pollutants is huge[1]. The emitted NO_X can form acid rain, photochemical smog, also cause the greenhouse effect[2, 3], and ultimately endanger human health. Therefore, it is imperative to control NO_X emissions during coal combustion. But the combustion of pulverized coal is very complicated, and the combustion of coke is the most influential link, therefore. Many studies have focused on the coke combustion stage[4]. Transition metal oxides also show excellent catalytic performance and can effectively promote the migration of fuel nitrogen to the gas phase[5]. Therefore, it can be boldly guessed that the metal additives also have a catalytic effect on the control of NO_X emissions during the combustion process. Zhao et al.[6] found that both Na and Fe loading reduced NO_X emissions during coke combustion. Zhong et al.[7] believed that iron can effectively catalyse the reduction of NO_X during the process of high temperature combustion of coal char and significantly reduce NO_X emissions. Literature[8] believed that different metals have different catalytic activity factors, and the catalytic activity of iron depends on temperature. Ce can change the reducibility of the catalyst surface to improve the catalytic activity. Current research is still focused on the effect of single-metal additives on combustion denitrification, and there is a lack of research on the combined effect of composite

metal additives on the combustion process. Therefore, this work has studied the effect of transition metals and rare earth metals in the combustion of co-catalysis NO_X reduction, and obtained the corresponding laws.

2 Materials and Methods

2.1 Coal sample modification

Select coking coal as the experimental sample. Firstly, because of the complex mineral composition of coal, in order to simplify the research, the demineralized coal was selected as the research object. In this paper, HCl-HF acid pickling was used to remove minerals, soak in a water bath at 60 °C for 4 hours, and rinse with deionized water until Cl^- is not detected, and demineralized coal is prepared. Next the coal was baked in an oven at 105 °C for about 6 hours. Then it is crushed and sieved to select a coal sample with a particle size of about 0.2mm. Afterwards, 1%, 2%, 3% and 4% Fe additives were loaded on the demineralized coal using a physical mixing method. Make the Fe additives and demineralized coal as homogeneous as possible.

2.2 Coke preparation

The pyrolysis was completed in a high-temperature tube furnace, the sample was heated at a rate of 10 ℃/min to 1000 ℃, and was subjected to high-temperature pyrolysis in an Ar atmosphere of 50 mL/min for 1 h, and then naturally cooled to room temperature. Finally, the coke is sieved to 40~80 mesh. The industrial analysis and

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elemental analysis of raw coal char (RC) and demineralized coal char (DC) are shown in Table 1. The nitrogen content of demineralized coke is higher than that of coke. This may because the minerals in coal promote the migration and emission of nitrogen-containing substances to gas during coal pyrolysis.

Table 1. The proximate analysis and ultimate analysis of raw char (RC) and demineralized char (DC)

	Proximate analysis (*wt* %)				Ultimate analysis (*wt* %)				
	M_{ad}	A_d	V_{daf}	FC_{ad}	C_{daf}	O_{daf}	H_{daf}	N_{daf}	S_{daf}
YC	0.15	9.99	1.78	88.08	79.09	19.12	0.23	1.16	0.40
DC	0.20	0.49	1.69	95.72	89.45	8.77	0.20	1.26	0.32

2.3 Experimental process

The combustion experiment was carried out in a tube furnace. Before each reaction, weigh about 0.5g of the coke, and place it in the middle constant temperature zone of the reaction tube, The Ar gas is flowed at a flow rate of 50 mL/min, and purge for 5 minutes to purge the air in the pipe, heat up to the combustion temperature required for the experiment, after the constant temperature is stable for 10 minutes, switch the O_2/Ar mixture, adjust the flow rate to 200mL/min, and the tail gas end is connected to a flue gas analyzer (KANE9506) for online detection of NO_X. After the experiment is completed, coal ash is collected, and XRD is used to characterize the crystal form of additives in the ash sample. Each experiment was repeated twice, and when the error of parallel experiment data was less than 2%, the average value was taken.

The amount of NO_X produced and the decrease ratio are shown in formulas (1) and (2).

$$m_{NO_X} = Q \times 10^{-6} \int_0^t C_{NO_X}(t)dt \qquad (1)$$

m_{NO_X} — the amount of NO_X produced by coke combustion, mg

Q — the volume flow of air, mL/min

C_{NO_X} — the mass concentration of NO_X in flue gas at time t, mg/m^3

$$\varphi = \frac{W_{NO_X(\text{coke}-0)} - W_{NO_X(\text{coke}-1)}}{W_{NO_X(\text{coke}-0)}} \qquad (2)$$

φ — the reduction ratio of NO_X of clean coke, %

$W_{NO_X(\text{coke}-0)}$ — the amount of NO_X produced during the combustion of coke, mg

$W_{NO_X(\text{coke}-1)}$ — the amount of NO_X produced during the combustion of clean coke, mg

3 Results & Discussion

3.1 Effect of iron loading ratio on NO_X emissions from demineralized coke combustion

When the demineralized coke with different iron loading ratios is burned separately, the NOx emission and decrease ratio are shown in Figure 1 and Figure 2, respectively. It can be seen from the Figure 1 that NOX emissions are negatively correlated with the temperature range, that is, as the temperature increases, the emissions decrease. It shows that increasing the temperature is beneficial to reduce NOX emissions. However, the higher the load, the better NOX reduction. When the load ratio exceeds 4%, the NOX emissions will be higher than 3% at the same temperature. And it can be seen from that the best temperature is 900 ℃, the emission of NOx of was calculated to be 1.18 mg.

In order to express the decrease of NOX by loading additives more vividly, compare the release of NOX in various proportions with the demineralized coke without additives. The decrease ratio at each temperature is shown in Figure 2. The calculation can be obtained at 900 ℃, 3% with the addition of Fe additives, the NO_X emission is 1.18mg, and the NO_X decrease rate is 60.5%. Under these conditions, the NO_X emission is the least. It can be inferred that a 3% Fe load has the best effect on catalytic reduction of NO_X release. Therefore, in this experiment, clean coke with a load of 3% Fe_2O_3 co-pyrolysis releases the least amount of NOx, which proves that this load of additives is most conducive to reducing the release of NO_X. Meanwhile, the catalytic effect of Fe in the NO-coke reaction is proved[9], that is, the addition of Fe_2O_3 is beneficial to promote the reduction of NO_X, thereby reducing the release of NO_X.

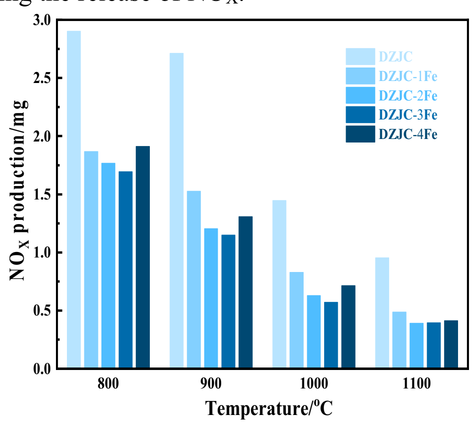

Figure 1. NO_X production with different iron loading ratio

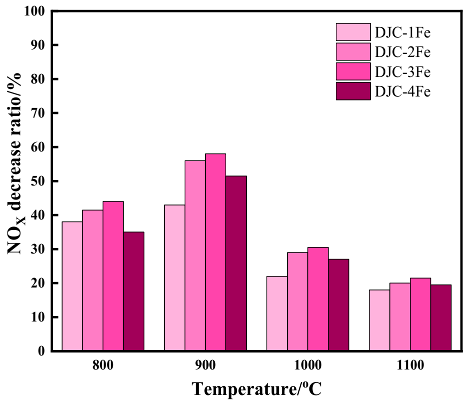

Figure 2. NO_X decrease ratio with different iron loading ratios

3.2 Effect of Fe-Ce composite ratio on NO_X emissions from demineralized coke combustion

The NO_X emissions and decrease ratio during the combustion process with different Fe-Ce composite ratios are shown in Figure 3 and Figure 4, respectively.

It can be seen from the figure that the effect of single additive CeO_2 loading is far less than that of single Fe_2O_3 loading. Compared with DC-3Fe and DC-3Ce, the NO_X emission of coke combustion under the composite auxiliary is reduced However, when the two metals are combined loading, the release of NO_X at (800-1100 ℃) is effectively reduced. When the recombination ratio is less than 2, the NO_X reduction rate increases with the increase of CeO_2 load, but a downward trend appears when the temperature rises to 1100 ℃. When the CeO_2 to Fe_2O_3 load ratio exceeds 2, the reduction of NO_X is directly related to the temperature, and this trend is proportional to temperature. The reduction of NO_X emissions from coke combustion after the composite addition of Fe and Ce oxide additives is more obvious, and the NO_X reduction rate of DJC-2FeCe is the highest, and the effect is the most significant. Therefore, the experimental results show that the doping of cerium is not always beneficial, and a small amount of doping of cerium is beneficial to further reduce combustion NO_X release on the basis of supporting iron-based additives.

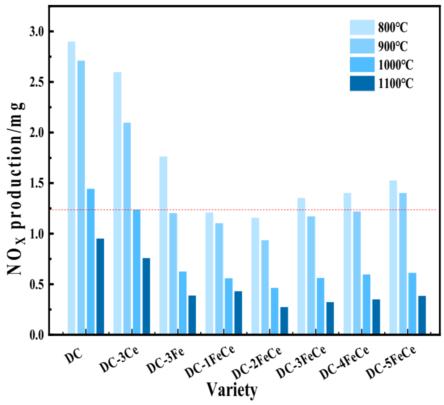

Figure 3. NO_X production with different iron loading ratios

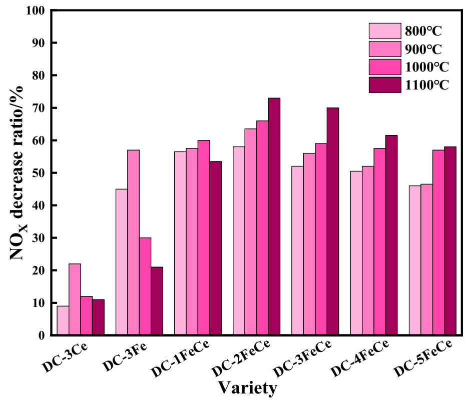

Figure 4. NO_X decrease ratio with different iron loading ratios

3.3 Effect of temperature on NO_X emissions during the combustion of demineralized coke with the optimum ratio of Fe-Ce

The NO_X emissions and decrease ratio during the combustion process of demineralized coke with Fe-Ce composite ratio of 2:1 are shown in Figure 5.

Obviously, during the combustion process, the NO_X emissions of demineralized coke with the optimal load ratio gradually decreases, which corresponds to a linear increase in the NO_X reduction rate. This shows that temperature is a key factor affecting combustion, and high temperature can significantly reduce NO_X emissions during combustion. When the combustion temperature increases to 1100 ℃, the amount of NO_X emitted by the coke is 0.28mg, and NO_X reaches 73%. This indicates that high temperature is beneficial to reduce the release of NO_X in coke. The literature[10] believes that as the high temperature time passes, the coke enters the burn-out stage, and the O concentration decreases. At this time, although the coke NO_X is continuously formed, it decomposes quickly at the same time, and part of the NO_X that has been generated is reduced by metal decomposed into N or N_2, Ce doping improves the reducibility of mixed oxides, resulting in a reduction in overall NO_X emissions.

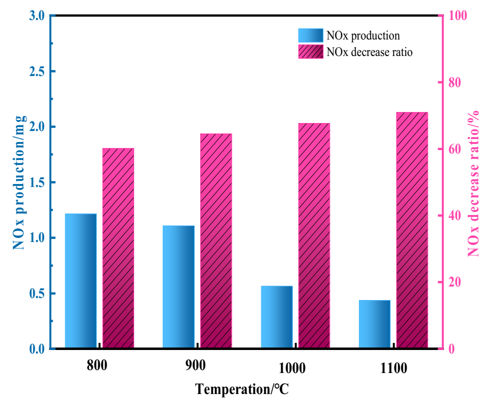

Figure 5. NO_X production and decrease ratio with 2FeCe

3.4 Phase morphology analysis of loading additives before and after coke combustion

The XRD analysis of the auxiliary agent in the demineralized coke and in the ash after combustion are shown in Figure 6 and Figure 7, respectively.

As shown in the Figure 6, XRD characterization analysis was carried out on the coke to determine the phase morphology of the auxiliary agent, the coke doped with Fe has obvious Fe_2O_3 and Fe diffraction peaks, and the intensity of the diffraction peaks is strong, which may be the reason for the low catalytic efficiency of crystalline iron oxide. After the co-doping of Ce, the peak strength of iron diffraction peak of each load auxiliary sample is still gradually weakening, which shows that the addition of Ce can effectively change the crystallinity of iron. Researches have shown[11] that when metal oxides interact, cerium oxide can promote the storage and release of oxygen improves the mobility of oxygen and forms surface and structural oxygen vacancies, thereby improving the redox properties of the catalyst[12].

In order to clarify the phase morphology of the composite additives after combustion, the burned ash was subjected to XRD characterization, the result is shown in Figure 7. Through the analysis of the ash content, it is found that the burned ash contains almost no other components, except for the added compound additives. Only the phase structures of iron and cerium are obtained by the characterization, and they are in their respective oxide forms after combustion, namely Fe_2O_3, CeO_2, and there are almost no elemental Fe compounds in the phase. This is related to the combustion reaction is a strong oxidizing system, and the composite assistant as a catalyst is finally oxidized under this oxidizing condition.

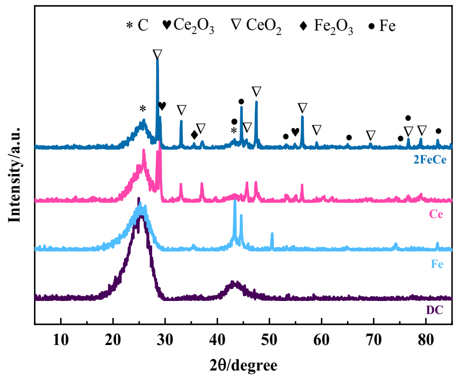

Figure 6. Fe-Ce phase transition law before combustion

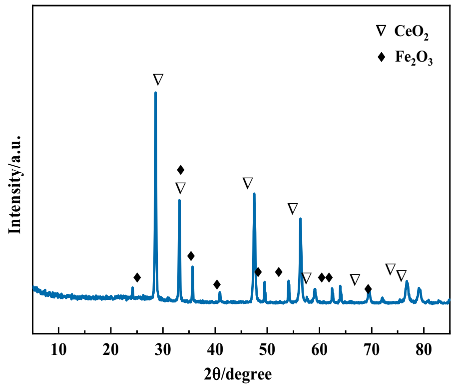

Figure 7. Fe-Ce phase transition law after combustion

4 Conclusions

The effect of composite metal promoters in the catalytic reduction of NO_X was studied in a high-temperature tubular furnace reactor. The results are as follows: In the combustion process of demineralized coke, the addition of metal additives can not only inhibit the production of NO_X, but also reduce the release of NO_X, and ultimately achieve lower NO_X emissions. During the combustion of coke, the catalytic effect of Fe-Ce composite is greater than that of iron or cerium alone. While the reaction temperature is 1000 ℃ and the addition ratio is 2:1, the catalytic effect on NO_X decrease ratio is optimal, the NO_X emissions is 0.28 mg, and the NO_X decrease ratio is 73%, which indicate that the modification by a proper amount of Ce doping is beneficial to further improve the effect of iron additives. The composite addition method can effectively reduce NO_X emissions and control air pollutants, which has important practical significance for achieving clean and efficient utilization of coal.

Acknowledgments

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