Control of the NOx emissions by metal additive in-situ catalyze the reduction of NOx during combustion

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Abstract. The emissions of NOx during combustion causes serious pollution to the environment. It is especially important to reduce NOx pollution during coal combustion through clean coal utilization. The use of civil clean coke, which is mainly prepared by mixing metal additives with coal, is one of the ways of clean coal utilization. In this work, a series of coke samples with loading metal additives were prepared by physical method, and the NOx emissions were investigated in a fixed bed reactor. The results show that Na, K, Mg, Ca, Cr, Fe, Co, Ni and Cu play in-situ catalytic effects on the NOx reduction reactions. It is of great practical value and scientific significance to the comprehensive treatment of NOx and the clean utilization process of coal.

1. Introduction

NOx is a major contributor to acid rain and photochemical smog[1]. In China, one of the important sources of NOx is the emissions of coal nitrogen during combustion. A lot of NOx pollution comes from the combustion of coal. In order to reduce NOx emissions, many Researchers have done a lot of research and found that the mineral matter in the coal suppressed the conversion of fuel-nitrogen to NOx[2,3]. Therefore, the use of metal additives to achieve low NOx emissions is one of the effective methods to reduce NOx emissions during coal combustion. It is believed in the literature[4] that the conversion of fuel-nitrogen to NOx is reduced due to the catalytic action of mineral in coal. It has been pointed out in the literature[5] that sodium additive can catalyze the reduction of NO and significantly reduce the NOx emissions during combustion. It has been found in the literature[6-8] that temperature had a great influence on the catalytic activity of alkali metals, which significantly affect the catalytic activity of different alkali metals in the heterogeneous reduction reaction between coke and NO. Many researchers have studied the catalytic reduction of NOx by alkali metals and alkaline earth metals, but have not studied the role of transition metals. Therefore, this work studied the catalytic effect of transition metal NOx reduction compared with that of alkali and alkaline earth metals and the system results were obtained.

2. Experimental

2.1. Modification of coke samples
The coking coal was selected as the experimental samples. The modification of coke was achieved by co-pyrolysis of metal additives with coal. The coal was pickled in a water bath with a mixed acid at 80 °C for 4 h. Then it was rinsed with deionized water until the Cl- was not detected by AgNO₃. At last, the demineralized coal (de-coal) was obtained. The proximate analysis and ultimate analysis of coal and coke were listed in Table 1. The ash content of demineralized coke (de-coke) was 0.18%, which proved that the mineral was removed. The nitrogen content of de-coke was lower than that of the coal due to the emissions of the nitrogen-containing gas during the pyrolysis process. The nitrogen content of de-coke was higher than that of the coke because the self-mineral in the coke promotes the emissions of the nitrogen-containing gas. The ash composition analysis of coal was shown in Table 2. The modified coke was prepared by adding 3% of Na, K, Mg, Ca, Cr, Fe, Co, Ni and Cu, respectively.

### Table 1. The proximate analysis and ultimate analysis of coal and coke

|          | Mart (wt %) | Ash (wt %) | Vol (wt %) | Fixed Carbon (wt %) | Carbon (wt %) | Hydrogen (wt %) | Nitrogen (wt %) | Sulfur (wt %) |
|----------|-------------|------------|------------|---------------------|---------------|-----------------|----------------|--------------|
| Coal     | 0.58        | 8.12       | 16.63      | 76.16               | 82.01         | 4.07            | 1.33           | 0.39         |
| Coke     | 0.15        | 9.99       | 1.78       | 88.08               | 79.09         | 0.23            | 1.15           | 0.40         |
| De-coke  | 0.20        | 0.18       | 2.65       | 96.97               | 89.45         | 0.20            | 1.26           | 0.42         |

### Table 2. The ash composition analysis of coal

| Constituent | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO |
|-------------|------|-------|-------|------|-----|-----|
| Content/wt.% | 50.34 | 31.4  | 9.85  | 1.31 | 1.23 | 3.28 |

2.2. Preparation of coke samples

The samples were heated at the ratio of 10 °C/min to 800 °C and the temperature was increased to 1050 °C at the ratio of 5 °C/min. At this temperature, the high-temperature distillation (pyrolysis) was performed for 1.5 h. Next, it was naturally cooled to room temperature. At last, it was ground and screened to the size between 0.2 mm and 0.5 mm.

2.3. Experimental method

The experimental apparatus was comprised of a gas supplying part, a fixed bed reactor (I.D. 10mm) and an on-line gas analysis part. For each run, samples (0.5 g) were packed into the fixed bed reactor and were heated to 800°C for 30 min in flowing Ar to prevent, and then the Ar was switched to a mixture gas flow of Ar/O₂. The composition of flue gas was monitored by an on-line gas analyzer, KANE9506 flue gas analyzer (England), for the concentrations of O₂ and NOx (sum of NO and NO₂). The precision for NO and NO₂ was 1 ppm, while the precision for O₂ was 0.1%. For each run, the initial O₂ concentration was always 21.0%. The NOx reduction ratio was expressed in equation (1).

\[
\eta = \frac{W_{NOx (coke - k)} - W_{NOx (coke - j)}}{W_{NOx (coke - k)}} \times 100\% \quad (1)
\]

\(\eta\) -- the reduction ratio of NOx of clean coke, %

\(W_{NOx (coke - k)}\) -- the production of NOx during combustion of coke, mg

\(W_{NOx (coke - j)}\) -- the production of NOx during combustion of clean coke, mg

3. Results and Discussion

### 3.1. Study on NOx emissions during the combustion of raw coal, coke and de-coke

The concentration and production of NOx emissions during the combustion of coal, coke and de-coke were shown in Figure 1 and Figure 2, respectively.
It can be seen from Figure 1 and Figure 2 that at the same temperature, the amount of NOx produced by coke combustion was less than that of raw coal, which indicated that high-temperature pyrolysis process can effectively reduce the emission of NOx. During the high-temperature pyrolysis, some nitrogenous substances volatilize in the form of NH₃, HCN. The residual non-volatile nitrogen residue in the pyrolysis existed in the form of coke-nitrogen and then reacted with O₂ to form nitrogen oxides during the combustion process.

In order to reduce the influence of minerals on the experiment, the de-coke was prepared by pyrolysis at high temperature. It can be seen from Figure 2 that the NOx emissions of de-coke significant increased compared to that of coke. The production of NOx of coal, coke and de-coke was calculated to be 2.74 mg, 1.73 mg and 2.90 mg, respectively. The increasing in NOx emissions during combustion of de-coke is related to the kinds and contents of minerals contained in the coal.

3.2. Effect of alkali metals on NOx emissions
The NOx production and decrease ratio of coke loaded with alkali metals at 800 ℃ were shown in Figure 3.

It can be seen from Figure 3 that loading different kinds of alkali metal compounds on de-coke can significantly reduce the emissions of NOx during coke combustion. This proved that the alkali metal can effectively catalyze the reduction of NOx. Different alkali metal compounds had different influences on NOx emissions. The NOx emissions of de-coke with Na-additive was 2.08 mg and the reduction ratio of NOx was 28%. The NOx emissions of de-coke with K-additive was 1.90 mg and the reduction ratio of NOx was 34%. The denitrification effect of K-additive was better than that of Na and, which is related to the alkalinity of two alkali metals. To some extent, alkali metal additives inhibited the heterogeneous oxidation of nitrogenous substances in coal and its coke and enhanced the
reduction of NO on in-situ coke\cite{9}. It has been proposed that alkali metals possessed an enhancing effect for the reaction, which was attributed to an increasing number of reaction sites via the catalyst dispersion\cite{10}.

3.3. Effects of alkaline earth metals on NOx emissions

The NOx production and decrease ratio of coke loaded with alkaline earth metals at 800 °C were shown in Figure 4.

![Figure 4. NOx production and decrease ratio of coke loaded with alkali earth metals](image)

It can be seen from Figure 4 that loading different kinds of alkaline earth metal compounds on de-coke can significantly reduce the emissions of NOx during coke combustion. This proved that the alkaline earth metal can effectively catalyze the reduction of NOx. Different alkaline earth metal compounds had different influences on NOx emissions. The NOx emissions of de-coke with Mg-additive was 2.24 mg and the reduction ratio of NOx was 23%. The NOx emissions of de-coke with Ca-additive was 2.09 mg and the reduction ratio of NOx was 25%. The denitrification effect of Ca-additive was better than that of Mg, which is related to the alkalinity of two alkaline earth metals. It was thought to be in the literature\cite{11} that the maximum emissions of NOx at high temperatures may result from the decomposition of Ca-N intermediates. The formation and the subsequent decomposition of Ca-N intermediate direct or govern the conversion of fuel-N towards NOx. However, the components of the Ca-N intermediates formed during combustion have not been determined by now.

3.4. Effects of transition metals on NOx emissions

The NOx production and decrease ratio of coke loaded with transition metals at 800 °C were shown in Figure 5.

![Figure 5. NOx production and decrease ratio of coke loaded transition metals](image)
It can be seen from Figure 5 that loading different kinds of transition metal compounds on de-coke can significantly reduce the emissions of NOx during coke combustion. This proved that the transition metal can effectively catalyze the reduction of NOx. Different transition metal compounds had different influences on NOx emissions. The catalytic NOx reduction properties of transition metals were Fe > Ni > Co > Cr > Cu and the reduction ratio of NOx were 42%, 40%, 37%, 31% and 15%, respectively. The catalytic effect of Fe-based metals was most significant. It was found in the literature\cite{12} that Fe\(^{3+}\) and Co\(^{3+}\) proved to be the active sites for CO and NO evolution, respectively: Co species promoted the transformation of COO\(^{-}\) to CO\(_3\)^{-} whereas Fe species promoted the generation of NO\(_3^{-}\). Additionally, metal or acid modification can also enhance the reaction of NO + CO over carbon-based materials\cite{13}.

4. Conclusions

The NOx reduction by the in-situ catalytic effects of metal additives was investigated in the fixed bed reactor. The following results were obtained. During combustion of modified coke, metal additives not only had catalytic effects on the reduction of NOx, but also suppressed the formation of NOx in coke combustion. The catalysis of the K-additive in the alkali metal was greater than that of the Na-additive. The catalytic effect of the Ca-additive in the alkaline earth metal was greater than that of the Mg-additive. The efficiency of catalyzing NOx reduction was related to its own alkali strength. The catalytic effect of Fe-additive in transition metals was most significant in this work. The catalytic effect of transition metals was best compared to the catalysis of alkali metals and the catalysis of alkaline earth metals. Under certain conditions of a load ratio of 3%, the catalytic effect of the Fe-additive was preferably at 800 ℃. The NOx emissions were 1.69 mg and the reduction ratio of NOx was 42%. This method can effectively control NOx pollution and has important practical significance for realizing efficient and clean utilization of coal.

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