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Effect of limestone on the emission of NO during petroleum coke combustion

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ABSTRACT

In order to investigate the effect of limestone on NO emission during petroleum coke combustion, experiments were conducted in a horizontal fixed-bed reactor connected with an on-line FTIR gas analyzer. Calcium based materials (limestone, CaO and $CaSO_4$) were employed as solid additives, while CO_2 and SO_2 were mixed with the carrier gas to research their effects on NO emission. The results showed that char-N was the most important source of NO. Char-NO, which was produced by the combustion of char-N was significantly promoted with the addition of limestone. This was mostly caused by the catalytic effect of CaO, which was produced by the decomposition of limestone. To clarify the mechanism, pyrolysis experiments were carried out, and the transformation of fuel-N to gaseous-N and char-N was investigated. The conversion ratio of fuel-N to gaseous-N was promoted to a higher value by the additives, whereas the proportion of char-N slightly decreased. However, most of fuel-N still remained in char regardless of additives. Therefore, it could be concluded that the conversion ratio of char-N to NO obviously increased due to the addition of additives and then resulted in an increase in the overall emission of NO during combustion. The nitrogen species in raw material and chars were analyzed using X-ray photoelectron spectroscopy (XPS). The results showed that the conversion route of fuel-N to char-N during pyrolysis was not obviously affected by limestone, however, it was greatly affected by CaO. More nitrogen was restrained in the form of N-X in chars produced by the co-pyrolysis of petroleum coke and CaO, due to which, the positive effect of CaO on NO emission was weaker than that of the limestone.

1. Introduction

Petroleum coke is produced in the process of petroleum refining, and is a kind of fossil fuel which is characterized by low volatile, low ash and high sulfur content. The yield of petroleum coke has increased year by year due to the increase in demand of oil. It is widely accepted that the circulating fluidized bed combustion (CFBC) is the most effective utilization approach of petroleum coke. Due to the environmental requirements, limestone is employed as a sorbent to capture SO_2 during the combustion of petroleum coke in a circulating fluidized bed boiler (CFBB) [1–7].

It is well-known that limestone can increase the emission of NO during coal combustion [8–12]. However, the effect of limestone on NO emission during the combustion of petroleum coke is not well understood. Generally, limestone suppresses the emission of NO during petroleum coke combustion [13–15]. Shimizu et al. [13] studied the effect of limestone on NO emission during petroleum coke combustion using a bench-scale bubbling fluidized bed combustor, and found that NO gradually decreased after limestone feed. They pointed that volatile-N was important in determining the emission of NO, and the reduction of NO was attributed to the deactivation of ash, which acts as a strong catalyst to form NOx from the volatile-N (NH_3). NO was also found to be suppressed by limestone addition during petroleum coke combustion in the experimental study of Brereton [14] conducted in a pilot-scale circulating fluidized bed combustion facility. However, contrary to the explanation given by Shimizu et al. [13], Brereton explained that the volatile content in petroleum coke was so little that the formation of NO catalyzed by limestone played a minor role, due to which, the reduction in NOx by CO or H_2 catalyzed by limestone dominated the combustion process. While in the work of Zhang et al. [15], NO first increased and then decreased with the increase of Ca/S during petroleum coke combustion in a 1 t/h fluidized bed boiler. This was due to the competing reactions of oxidation of fuel-N and reduction of NO by CO, both of which were catalyzed by calcined limestone. In conclusion, there are significant differences in the results and explanations given by previous researches.

Besides, a few researchers have tried to investigate the effect mechanism of limestone on NO formation and reduction experimentally

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and theoretically. Zijlma et al. [16] investigated the oxidation of NH_3 over partially sulphated limestone based on experimental work conducted in a fixed-bed reactor and modelling work. They found that the oxidation of NH_3 to NO was strongly catalyzed by CaO, and the formation of NO decreased with increasing CaO conversion to less active $CaSO_4$. However, the formation of N_2 was almost not influenced. Therefore, they pointed out the decrease in NO formation was due to the increasing conversion of CaO to $CaSO_4$, not the result of NO reduction by NH_3. While in the work of Kiil et al. [17] where a theoretical study was conducted, the reduction of NO by NH_3 over $CaSO_4$ was found to be important. With the increasing conversion of CaO to $CaSO_4$, the oxidation of NH_3 to NO catalyzed by CaO decreased and the reduction of NO by NH_3 over $CaSO_4$ increased. Hansen et al. [18] researched the effect of limestone, the surface of which changed continuously between CaO, CaS and $CaSO_4$, on the reduction of NO by experiments carried out in a laboratory scale fixed bed quartz reactor. The results indicated that CaS and CaO were active catalysts for reduction of NO by CO, while $CaSO_4$ and $CaCO_3$ were poor catalysts. However, it should be noted that researches discussed above do not provide definite conclusions regarding the combustion of petroleum coke.

Additionally, the effect of CO_2 on fuel nitrogen conversion during pyrolysis of petroleum coke, which is the first step of combustion, was studied in a fixed bed reactor [19]. The research showed that CO_2 suppressed the nitrogen release into the gases phase (volatile-N) at lower temperature, while it enhanced the conversion from fuel nitrogen to NOx precursors at higher temperature.

A review of literature shows that the effect of limestone on NO emission during petroleum coke combustion and its mechanism are still not clear. The combustion of petroleum coke with desulfurization using limestone in CFBB is very complicated due to the presence of gas-solid multiphase. Therefore, it is difficult to find the factor by which the emission of NO was really affected. In the present work, combustion experiments were conducted in a horizontal fixed-bed reactor to study the effect of limestone on NO emission. CaO and $CaSO_4$, produced by the addition of limestone during the desulfurization process, were employed as additives. The effects of CO_2 and SO_2, whose concentration could be influenced by the addition of limestone, were also considered. Besides, to further understand the mechanism of NO emission, the conversion of fuel-N to gaseous-N and char-N during the pyrolysis of petroleum coke were studied. The nitrogen species in raw material and in chars were analyzed using XPS. The relationship between char-N species and NO was also investigated.

2. Experimental

2.1. Materials

In this work, petroleum coke produced at a large-scale petroleum refining company located in eastern China was employed as fuel. Results from its proximate and ultimate analysis are presented in Table 1. It can be seen that the petroleum coke was characterized by low volatile content, low ash content, and high sulfur content. The average particle size of the fuel was 250 μm. The petroleum coke sample was dried for 2 h at 105 °C to remove moisture.

Limestone consisting of 99.7% $CaCO_3$ was used as SO_2 sorbent. Its average particle size was about 297 μm. Calcium oxide (CaO) and calcium sulfate ($CaSO_4$), which were additionally introduced by adding limestone, were employed as the additives. CaO was produced by the decomposition of limestone at the same temperature as petroleum coke combustion. $CaSO_4$ was procured as a commercial reagent having purity of 99.99%.

Table 1
Proximate analysis (ar, wt%) and ultimate analysis (ar, wt%) of petroleum coke.

Proximate analysis				Ultimate analysis				
M_{ar}	A_{ar}	V_{ar}	FC_{ar}	C_{ar}	H_{ar}	N_{ar}	S_{ar}	O_{ar}
0.63	0.26	9.69	89.42	84.22	3.5	1.04	7.02	3.33

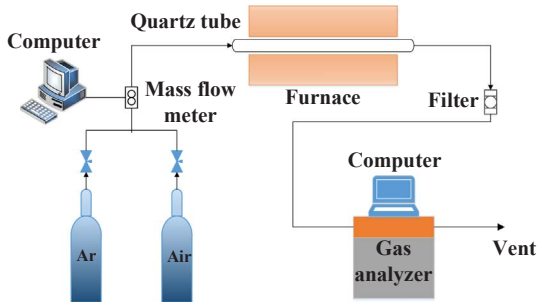

Fig. 1. Schematic of the experimental setup consisting of a horizontal fixed-bed reactor.

2.2. Methods

Experiments were conducted in a horizontal fixed-bed reactor. Fig. 1 shows the schematic of the experimental setup. The furnace was 800 mm long with the inner diameter of 60 mm. The quartz tube was 1000 mm long with the inner diameter of 36 mm. The temperate of the reaction zone was controlled using an electric furnace with a temperature controller, the monitoring point of which was set inside the quartz tube, where the solid materials were placed to ensure an accurate temperature control. All of the experiments were conducted at 900 °C, the conventional temperature for the combustion of petroleum coke in a CFBB, 1 atmos. Air (21% oxygen and 79% nitrogen) or argon (Ar) having purity of 99.999% was used as the carrier gas. The gas flow rate was controlled using mass flow meters. Before experiments, the additives were evenly mixed with petroleum coke in a certain Ca/S molar ratio, respectively. Then, the mixed samples were placed into the quartz boat with a thickness less than 1 mm. During each test, the reactor was first heated to 900 °C and then maintained for 15 min. After that, the quartz boat (with length of 100 mm, width of 25 mm and thickness of 1 mm) that contained the samples was rapidly pushed into the reaction zone. Each experiment was repeated three times to make sure that the relative standard deviations were less than 3%.

2.2.1. Petroleum coke combustion

100 mg petroleum coke was employed in each combustion experiment. The air flow rate was maintained at 1 L/min. In order to ascertain the same molar ratios of additives, the weights of CaO and $CaSO_4$ were calculated based on that of limestone. The additives were mechanically mixed with petroleum coke, and the calcium to sulfur molar ratio was varied from 0:1 to 4:1, respectively.

The flow rate of CO_2 or SO_2 (purity of 99.99%) was varied from 0 to 30 mL/min, and was added into the carrier gas to investigate the influence on NO emission.

The concentrations of CO_2, SO_2 and NO in the flue gas were measured on-line by a gas analyzer (Horiba PG-350, Japan). The measurement frequency of the analyzer was set to be 3 s.

2.2.2. Petroleum coke pyrolysis

The pyrolysis experiments of petroleum coke were conducted in the horizontal fixed-bed reactor and the effects of additives on the conversion of fuel nitrogen were investigated. In these experiments, 100 mg petroleum coke was employed. The flow rate of Ar was maintained at 1 L/min to make sure that the flue gas would have the same residence time as in the combustion experiments. In the work of Shimizu et al. [13], the pyrolysis temperature was set to be 300 °C higher than that of the combustion in order to simulate the rise in