



# Release of nitrogen oxides during combustion of model coals



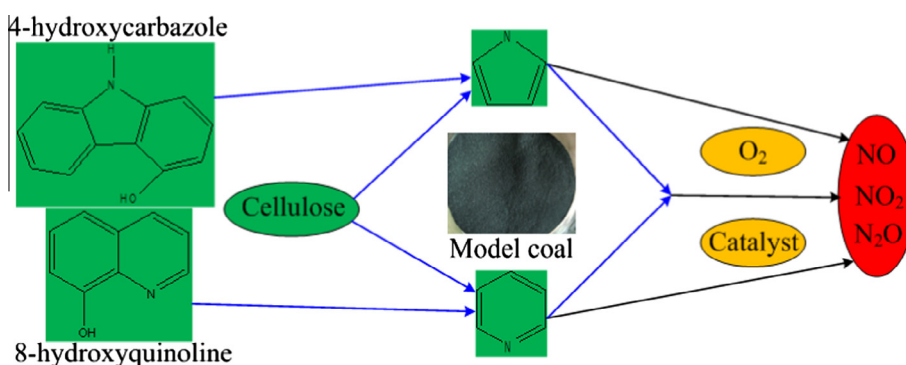
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## HIGHLIGHTS

- Two model coals, containing pyrrole or pyridine, are burned in an entrained flow.
- NO is the dominant species, and small amounts of NO<sub>2</sub> and N<sub>2</sub>O are also released.
- The interaction between pyrrolic and pyridinic nitrogen influences the NO release.
- Na, Ca and Fe promote NO release for pyrrole but suppress NO release for pyridine.
- NO release rises with increasing oxygen concentration first and then decline.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To study nitrogen oxides release, two model coals, which contain pyrrolic or pyridinic nitrogen, are prepared and burned in an entrained flow combustion system during 800–1300 °C. The influences of temperature, mineral, interaction between the two nitrogen forms, and oxygen concentration are discussed. The results show that NO is the dominant species, and its release increases drastically as temperature rises. N<sub>2</sub>O is only detected at 800 and 900 °C. The interaction between the two nitrogen forms gives rise to an increase of NO release at low temperatures but a decrease at high temperatures. For pyrrolic nitrogen, Ca and Na promote NO release above 900 °C, and Fe increases NO release for all temperatures investigated. As for pyridinic nitrogen, all minerals inhibit NO release above 900 °C. The NO release decreases when catalyst load rate increases. NO release rises with increasing oxygen concentration first and then decline. More NO<sub>2</sub> is released when oxygen concentration is above 20%.

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## 1. Introduction

The energy consumption of China placed an excessive reliance on coal, which has already caused serious environmental problems. The nitrogen oxides (NO<sub>x</sub> and N<sub>2</sub>O) can either be involved in photochemical smog and acid rain formation (NO<sub>x</sub>) or be implicated in the ozone layer depletion (N<sub>2</sub>O) [1]. NO<sub>x</sub> (NO and NO<sub>2</sub>) can also contribute to haze pollution events [2,3], which are of most

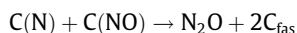
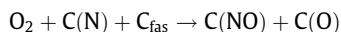
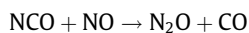
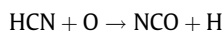
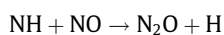
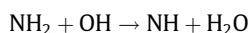
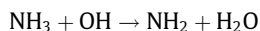
concern to the Chinese government and people nowadays. To alleviate environmental pollution, the Chinese Ministry of Environmental Protection promulgated a stringent limit for nitrogen oxides emission [4]. Therefore, much attention should be devoted to the reduction of nitrogen oxides emission.

According to three distinct formation mechanisms, NO<sub>x</sub> can be conceptually divided into three types: fuel NO<sub>x</sub>, thermal NO<sub>x</sub> and prompt NO<sub>x</sub> [5]. During combustion of pulverized coal, fuel NO<sub>x</sub>, which accounts for more than 80% of the total NO<sub>x</sub> emitted, is released from fuel nitrogen [6]. While the other two types of NO<sub>x</sub> originate from the nitrogen in the combustion air [5]. As for N<sub>2</sub>O,

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a consensus has not yet to be reached on the formation mechanisms. In general, the  $\text{N}_2\text{O}$  emission mainly occurs at low temperatures (727–1027 °C) and the  $\text{N}_2\text{O}$  formation pathways include homogeneous and heterogeneous reactions [7–9]



where  $\text{C}(\text{O})$ ,  $\text{C}(\text{N})$  and  $\text{C}(\text{NO})$  are the oxygen and nitrogen species on the char surface, and  $\text{C}_{\text{fas}}$  is a free active site. Whether during homogeneous or heterogeneous reaction processes, the fuel nitrogen and the  $\text{NO}$  make the main contribution to  $\text{N}_2\text{O}$  formation. In the corresponding low-temperature range, the nitrogen in the combustion air makes a small contribution to the total emission of  $\text{NO}$ , which means that  $\text{N}_2\text{O}$  mainly originates from the fuel nitrogen. On the whole, conversion of the fuel nitrogen constitutes the dominant source of nitrogen oxides. Hence, a good knowledge of fuel nitrogen transformation during coal combustion is essential to minimize nitrogen oxides emission.

Many efforts have been undertaken to investigate the nitrogen oxides emission from fuel nitrogen during combustion of various coals. The coal structure is extremely complex. Many functional groups, combustion products and minerals in coal could have significant influences on nitrogen oxides emission. Thus, the mechanisms of thermally induced fuel nitrogen transformation might be concealed when coal is taken as the research object. In order to avoid these limitations and gain an insight into the release of nitrogen oxides, model compounds have been used by several investigators [10–12]. The model compound is a pure substance, which has high nitrogen content and specific nitrogen functional group. Using model compound can make the results of catalysis research more precise because the catalysts can be loaded accurately. Furthermore, in contrast with coal, model compound simplifies the macromolecule and keeps the primary property and structure of the aromatic heterocyclic ring. Thus, the model compound is more suitable for mechanism study [13–15].

Three types of model compounds have been employed for the mechanism study of nitrogen release, including heterocyclic compounds, polymers and model coals. Heterocyclic compounds, such as pyridine, pyrrole, and quinolone, are usually liquid substances under room conditions. Polymers, such as polyvinylpyrrolidone, polyvinylpyridine and polyvinylcarbazole, contain pyridinic or pyrrolic nitrogen. Model coals are synthesized from phenolic nitrogen compounds and cellulose through compaction heat-treatment, which is a process for simulating the natural coalification [16]. Compared with the other two types of model compounds, model coals are more similar to coals in term of chemical structures and physical properties [16]. Many researchers have studied the transformation mechanism of fuel nitrogen from pyrolysis or combustion of heterocyclic compounds [10–15] or polymers [17–19]. However, less attention [16,20] has been focused on fuel nitrogen evolution from model coal pyrolysis. To our knowledge, nitrogen oxides emission from combustion of model coals has not been reported.

In order to investigate fuel nitrogen emission from different nitrogen functional groups, Wu et al. [16,20] prepared two model

coals. Temperature-programmed pyrolysis was performed in a fixed bed reactor up to 800 or 1000 °C. Whereas under the condition of pulverized coal boilers, coal pyrolysis and combustion take place rapidly in an entrained flow and at higher temperatures. As for the influence of minerals on nitrogen species emission, either coals [6,21,22] or model compounds [16,20,23] are taken as the objects, researchers preferred to perform the investigations in the fixed bed reactor. Combustion in an entrained flow condition has seldom been studied. Pyrrolic, pyridinic and quaternary nitrogen are the main nitrogen forms in coals. Quaternary nitrogen was believed to from  $\text{NH}_3$  during pyrolysis [24]. While pyrrolic and pyridinic nitrogen, which are more abundant than quaternary nitrogen, have attracted more attentions. Several studies [10–12] have reported nitrogen oxides emission during combustion of pyridinic or pyrrolic nitrogen with respect to heterocyclic compounds and polymers. These two most abundant nitrogen functional groups may have interactions during coal combustion. Unfortunately, the influence of these interactions on nitrogen oxides emission has rarely been investigated. Air staging and fuel staging (reburning) are two main low  $\text{NO}_x$  combustion technologies. A reducing zone under fuel-rich conditions will be established when staged combustion technologies are applied [25]. Oxygen enhanced combustion, and full oxy-fuel combustion has been broadly used in cement, metal, glass and incineration industries [26,27]. Currently, oxy-fuel combustion seems to be a prospective technology, which could be used in a pulverized coal-fired boiler. It is meaningful to evaluate the influence of oxygen concentration on nitrogen oxides emission.

Na, Ca and Fe are widely applied as catalysts to examine the influence of minerals on  $\text{NO}$  release from combustion of coals [21,22] and model compounds [23]. Mineral species can be loaded through two different methods, including impregnation [21–23] and physically mixing [21]. The former method can lead to a higher degree dispersion of catalyst, which could simulate the inherent minerals of coals better. According to Li et al. [28], this method has a risk of changing the coal structure significantly. The latter method is much easier to be implemented, which might provide a possibility to develop a new  $\text{NO}_x$  control technology in commercial boilers [22,29,30].

In this study, a combustion system with an entrained flow is built to simulate conditions in pulverized coal boilers. Two model coals, which contain pyridinic or pyrrolic nitrogen functional group, are used to investigate the nitrogen oxides release during combustion in a wide range of temperature. The influences of combustion temperature, mineral, the possible interaction between the two nitrogen forms, and oxygen concentration, are discussed in detail. Minerals are loaded through physically mixing.

## 2. Materials and methods

### 2.1. Sample preparation

Two model coals, which contain well-defined nitrogen functional groups, are used in this study. The synthesization and preparation of the model coals, which are similar to the methods of Wu et al. [16,20], have been described in our earlier work [31]. The model coal samples are ground and sieved to 63–98  $\mu\text{m}$ , and then air-dried at 105 °C for 24 h. The results from X-ray photoelectron spectroscopy (XPS) analysis have shown that nitrogen forms in model coal samples are totally pyridinic nitrogen (N-6) or pyrrolic nitrogen (N-5) [31]. Accordingly, these two model coal samples are denoted as M6 and M5 hereinafter.

As reported in our earlier work [31], comparisons of appearance, specific surface area, pore volume, proximate and ultimate analyses, and pyrolysis reactivity among these two model coals

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