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Influence of CaO on urea pyrolysis in the selective non-catalytic reduction $deNO_x$ process

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ABSTRACT

CaO affects urea pyrolysis when coalescing with melting urea, which decreased the performance of urea-SNCR $deNO_x$ process. The influence of CaO on urea pyrolysis was studied with a thermogravimetric analyzer, a fixed bed reactor, and DRIFTS. The mechanism of CaO was also analyzed. Experimental results showed that CaO decreased the pyrolysis rate of urea, especially in the presence of O_2. NH_3 production in urea pyrolysis was not influenced by CaO, whereas HNCO in the gaseous products disappeared and CO_2 production was increased remarkably. NO, N_2O, and CO were also produced in the presence of O_2. DRIFTS experiments showed that $Ca(NCO)_2$ and $CaCN_2$ were produced and the composition of the solid products varied with the atmosphere. Mechanism analysis showed that CaO initially reacted with melting urea and biuret to produce $Ca(NCO)_2$ and release NH_3 and H_2O. $Ca(NCO)_2$ decomposed to $CaCN_2$ and CO_2 with increasing temperature, and $CaCN_2$ can exist stably in the absence of O_2 because of its high thermostability. In the presence of O_2, $Ca(NCO)_2$ can be oxidized to N_2O, CO_2, and N_2, whereas $CaCN_2$ can be oxidized to NO, CO, and N_2.

1. Introduction

Nitrogen oxides (NO_x) are important air pollutants. Cement kilns and circulating fluidized bed boilers (CFBBs) are the main emission sources in China [1,2]. Selective non-catalytic reduction (SNCR) technology is the most suitable technology for cement kilns and CFBBs [3,4], in which NH_3 reacts with NO_x in the flue gas and reduces it to N_2 in a suitable temperature range. Besides NH_3, urea is another important reducing agent since it can convert to NH_3 by pyrolysis [5,6]. Urea has been widely used in different SNCR devices because of its low cost and high safety.

Pre-calciner and cyclone are suitable positions for SNCR technology in cement kilns and CFBBs. In urea–SNCR $deNO_x$ process, urea–water–solution droplets are injected into high temperature atmosphere; undergo water evaporation, urea melting, and pyrolysis [7–9]; and eventually become NH_3 and HNCO [10,11]. HNCO reacts with H_2O to produce NH_3 and CO_2. Previous studies [12–14] showed that high–concentration CaO in pre-calciner and cyclone [15–17] catalyzes NH_3 oxidation to NO and reacts with HNCO to NO and N_2O, resulting in the reduction of SNCR $deNO_x$ efficiency. Furthermore, CaO in the flue gas might run into and mix with melting urea and influences urea pyrolysis [18]. Thus, the influence of CaO on urea pyrolysis must be considered in urea–SNCR $deNO_x$ process applied in cement kilns and CFBBs.

Urea is heated and pyrolyzed after injection into high–temperature flue gas; thus, thermogravimetric analysis (TGA) is usually used to study urea pyrolysis. On the basis of weight loss and solid products, urea pyrolysis can be divided into four stages [19]: urea decomposition and polymerization to biuret, biuret conversion to cyanuric acid (CYA), CYA decomposition, and ammelide and ammeline decomposition. However, limited studies analyzed the influence of CaO on urea pyrolysis. Sang [20] studied urea–SNCR $deNO_x$ process in a fluidized bed reactor and found that CaO remarkably decreased the $deNO_x$ efficiency. Their results indicated that CaO can influence urea pyrolysis or catalyze NH_3 and HNCO oxidation. Krocher [21] tested materials for urea hydrolysis in a fluidized bed reactor and found that Al_2O_3 and TiO_2 exhibited high catalytic activities, which suggested that metal oxides are active in urea decomposition. Li [22] studied the influence of metal oxides on urea alcoholysis and found that metal oxides catalyzed urea decomposition to form isocyanate species, which is the key step in urea alcoholysis. Klimova [18] studied the pyrolysis of fertilizer-grade urea covered with dolomite and limestone through TGA in the range of 20–850 °C; results showed that isocyanic acid can react with CaO to form isocyanate, which can be oxidized by O_2. However, the gas products were not quantitatively measured, and the solid products were not analyzed. Therefore, the mechanism of CaO remains unclear.

Urea pyrolysis is influenced by CaO, although the effect and mechanism of CaO are unclear. Thus, verifying the effect and mechanism

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of CaO is important for the application of urea–SNCR deNO$_x$ process in cement kilns and CFBBs. The effect of CaO on urea pyrolysis was studied using TGA and a fixed reactor; the mechanism was analyzed in consideration of the DRIFTS measurement. The results can support the application of urea–SNCR deNO$_x$ process.

2. Experimental setup

The influence of CaO on the weight loss in urea pyrolysis was analyzed through TGA (TA Q500) was used to study. Analytically pure urea and CaO were used in the experiments. CaO was calcined for 1 h at 900 °C to maintain the properties stable during the heating process. CaO and urea (15 mg each) were well mixed and loaded on the bottom of the Pt pan of TGA. In the TGA experiments, N_2 was used as balance gas and the heating rate was set at 10 K/min. O_2 concentration was 5% in the conditions with the presence of O_2. The weight loss proportion of urea in each stage was calculated as Eq. (1).

$$\text{Weight loss proportion} = \frac{\text{weight loss in each stage}}{\text{original weight of urea}} \times 100\% \qquad (1)$$

A fixed bed reaction system was used to measure the gaseous products in urea pyrolysis, as shown in Fig. 1. The quartz reactor consisted of an external and an internal; and a quartz pan with a diameter of 15 mm was placed on top of the internal part. The quartz reactor was inserted into the constant temperature zone of an electric furnace. The reactant amount and heating rate were the same as those in the TGA experiments. N_2 was used as a balance, and the flow rate was 2.5 L/min. The controlling thermocouple was fixed at the bottom of the quartz pan to control the temperature of the sample bed. The concentration of the gaseous products was measured using a Fourier transform infrared spectroscopy (FTIR, Nicolet 6700). The FTIR was equipped with a ZnSe window and a MCT detector cooled by liquid nitrogen. The gas cell of FTIR was set at 150 °C to avoid the adsorption of the sample gas. The resolution of FTIR for gas measurement was 0.5 cm^{-1} and the scan number was 16 for a spectra. The FTIR was calibrated by standard gas using the method proposed by Li [23] and HNCO was measured using the bands between 2267.8 ~ 2269.5 cm^{-1}.

The solid products between urea and CaO were prepared using TGA; the DRIFTS spectra of the products were obtained with a Pike accessory. The resolution of the spectra was 4 cm^{-1} and the scan number for the spectra was 100.

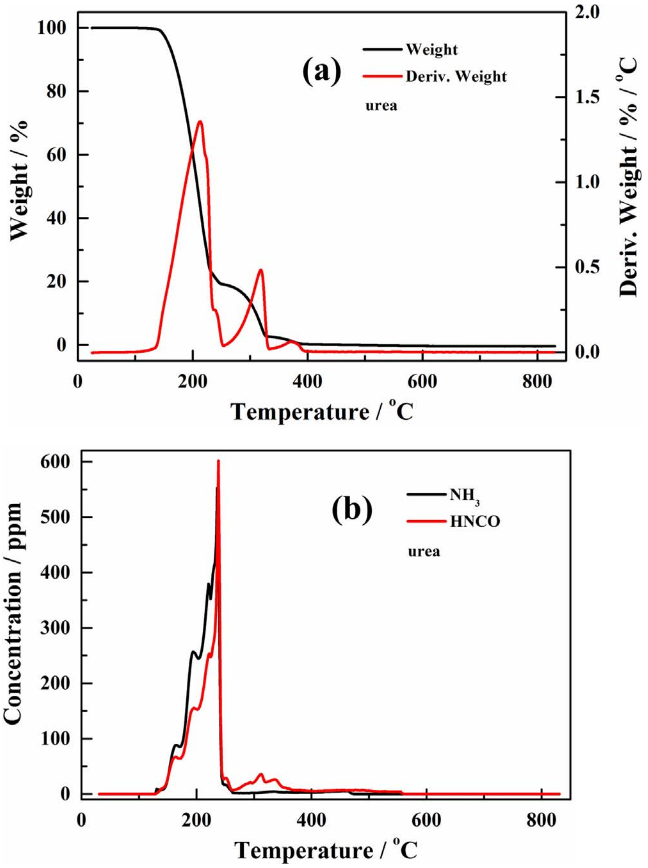

Fig. 2. Weight loss and gaseous products of urea pyrolysis in the absence of O_2. (a) weight loss, (b) gaseous pyrolysis products.

3. Results and discussion

3.1. Influence of CaO on urea pyrolysis in the absence of O_2

The weight loss and gaseous products of urea pyrolysis are shown in Fig. 2(a) and (b). Experimental results showed that urea pyrolysis mainly occurred below 360 °C and the main products were NH_3 and HNCO. According to the weight loss and the intermediate products [19], urea pyrolysis can be divided into four stages.

The first stage of urea pyrolysis was from room temperature to

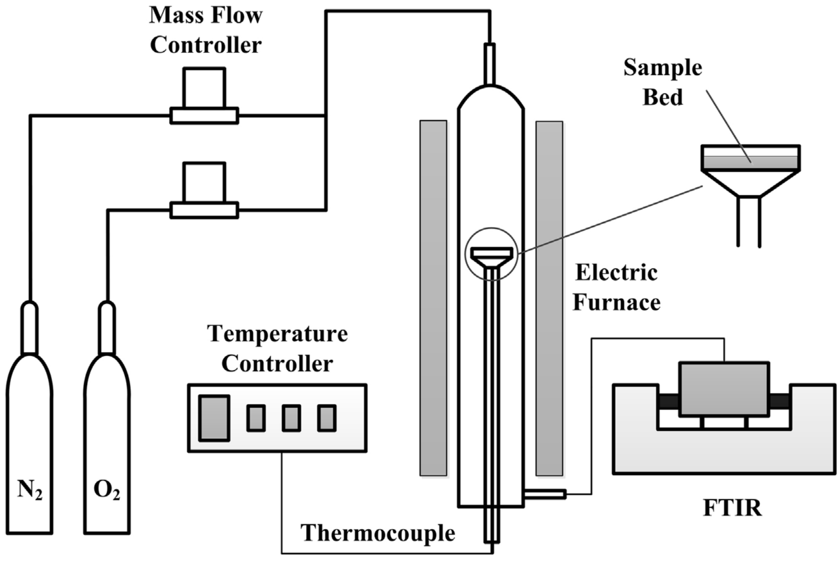

Fig. 1. Schematic of the fixed-bed experimental system.