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Catalytic effects of Fe, Al and Si on the formation of NO_X precursors and HCl during straw pyrolysis

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Abstract The catalytic effects of iron, aluminum or silicon on the formation of NO_X precursors (HCN, NH_3 and HNCO) and HCl during wheat straw pyrolysis were studied using a thermogravimetric analyzer (TG) coupled with a Fourier transform infrared (FTIR) spectrometer in argon atmosphere. The results show that the presence of iron, aluminum or silicon decreases conversion of straw-N into NH_3 with the sequence of Fe > Si > Al. The iron or silicon addition suppresses N-conversion into HCN and HNCO, and the aluminum addition has no notable influence on HCN emission during pyrolysis. The share of N-conversion to NH_3 and HCN increases, but that to HNCO and NO decreases a little in the presence of added iron, aluminum or silicon. The addition of SiO_2 results in the highest HCl removal efficiency.

Keywords Catalysis · HCl emission · NO_X precursor · Pyrolysis · TG-FTIR · Wheat straw

Introduction

Emissions of NO_X and N_2O from biomass power generation contribute to the formation of photochemical smog and acid, and to the enhancement of greenhouse effects [1, 2]. The nitrogen in biomass is converted into NO_X precursors such as HCN, NH_3 and HNCO as well as the nitrogen in char and the nitrogen in tar during pyrolysis. The conversion rate of those NO_X precursors into NO_X/N_2O depends strongly on the type of NO_X precursor. Much attention has been focused on NO_X reduction with the development of power generation using biomass in order to meet increasingly strict environmental standards. Clearly, the reduction in the NO_X/N_2O emissions would rely on the understanding of the formation of NO_X precursors during pyrolysis.

Proteins and amino acids are the main source of nitrogen in biomass [3, 4]. There are two ways to investigate the formation of NO_X precursors converted from either biomass itself or nitrogen-containing model compounds such as amino acids and proteins [5–9]. The mechanism how the nitrogen in biomass is converted into NO_X precursors during pyrolysis is imperfectly understood at present. In biomass pyrolysis studies, both HCN and NH_3 were usually found. In some studies, more ammonia than HCN was found and in some cases the opposite was true. HNCO formation during coal pyrolysis was always neglected [10–13], but it was detected during biomass and amino acid pyrolysis [3, 5, 8, 14]. Restricted by the analysis method usually used to quantify NH_3 (i.e., wet chemical analysis) [5, 6, 15], however, the formation of HNCO, a precursor to N_2O [1, 3, 16], has not been thoroughly investigated so far. So the formation of HNCO during fuel pyrolysis is not negligible and further research is highly needed.

The firing of pure straw is characterized by high-temperature corrosion and relatively high emissions of HCl due to the relatively higher chlorine content in straw. Chlorine in straw exists in both organic and inorganic forms. During combustion or gasification, organic chlorine is converted into HCl and released as a gas. Chlorine released from combustion and gasification has harmful effects on the environment [17]. Calcium-based material is generally used for HCl removal [18–20]. But the effect of

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mineral matters such as Fe, Al or Si on chlorine emission during straw pyrolysis is unknown.

The main elemental constituents of biomass minerals are Si, K and Ca with smaller amount S, P, Fe and Al. They occur as oxides, silicates, carbonates, sulfates, chlorides and phosphates in biomass [21]. In our previous work, alkali and alkaline earth metals, potassium and calcium have great and different effects on the formation of nitrogen species during biomass pyrolysis [9]. However, few studies have been carried out to analyze the influence of mineral matters on the formation of NO_X precursors and HCl with taking the mineral elements such as Al, Si, Fe, etc. in consideration.

Most previous researches studied the release of nitrogen species or HCl from biomass and coal pyrolysis under a specific temperature without continuous collecting and analyzing the products. The aim of this study is to use TG-FTIR analysis to reveal the catalytic effects of Fe, Al and Si on the release characteristics of NO_X precursors continuously and the distribution of nitrogen species during straw pyrolysis. Meanwhile, the effects of Fe, Al or Si on HCl removal rate were studied.

Experimental

Wheat straw (WS) was selected as the straw sample. The samples were ground into 0.5 mm (mean particle size) in diameter. Table 1 shows the proximate and ultimate analysis of the wheat straw sample.

Demineralization

The method of the demineralization was according to Wu et al. [22]. Wheat straw was demineralized by deionized water for 8 h. The demineralized samples were dried in a drying oven at 105 °C for 12 h (WS-de1). The mineral constituents of the raw wheat straw and demineralized sample were analyzed and listed in Table 2.

Table 2 The mineral constituents of the samples (mg/g)

Sample	K	Na	Ca	Fe	Al	Mg	Ti
WS	11.10	0.41	6.40	1.60	1.10	1.90	0.05
WS-de1	4.10	0.35	4.60	0.67	0.61	1.30	0.03

Catalyst impregnation

Fe_2O_3, Al_2O_3 and SiO_2 were used as the catalysts. The WS-de1 was immersed with aqueous solution of Fe_2O_3, Al_2O_3 or SiO_2, respectively. The mixtures were stirred in concentrated suspension for 8 h at room temperature. Finally, the mixtures were dried in the drying oven at 105 °C for 12 h. The dosing ratio of Fe_2O_3, Al_2O_3 or SiO_2 in the samples was 5% (mass %). Each of three kinds of samples treated is labeled as WS-de2, WS-de3 and WS-de4, respectively.

Pyrolysis and product analysis

Pyrolysis experiments were carried out with a TG analyzer (TGA 92). Powdered biomass sample of around 8 mg was pyrolyzed at heating rate of 40 °C min^{-1} from room temperature to 800 °C. Argon with purity of 99.999% was used as the carrier gas to provide an inert atmosphere for pyrolysis in order to eliminate the influence of atmosphere on the formation of nitrogen species and to remove the gaseous and condensable products. Evolved gases from TG were connected to a Bruker Vector 22 FTIR spectrometer through a heated (about 180 °C) transfer-line.

According to Lambert-Beer's law, the HCl concentration was determined based on the integral values of HCl releasing curves under specific IR absorption 2798 cm^{-1} [18]. The concentrations of HCN, NH_3, NO and HNCO were determined based on the integral value of HCN, NH_3, NO and HNCO release curves under specific IR absorptions 714 cm^{-1}, 966 cm^{-1}, 1900 cm^{-1} and 2251 cm^{-1}, respectively. Detailed information about the TG-FTIR apparatus and gaseous product analysis method can be referred to [9].

The mineral constituents of the samples were analyzed with inductively coupled plasma atomic emission spectrometer (Prodigy ICP-AES).

Results and discussion

Pyrolysis characteristics

Mass loss (TG) curves and corresponding derivative thermogravimetric (DTG) curves for straw with different

Table 1 Ultimate and proximate analysis of the sample (mass %)

Proximate analysis			Ultimate analysis (dry ash free basis)					Cl
Fixed carbon[a]	Ash[b]	Volatile[a]	C	H	S	O[c]	N	
14.20	8.90	85.80	48.32	2.54	0.11	48.21	0.82	0.68

[a] Dry ash free basis; [b] dry basis; [c] by difference

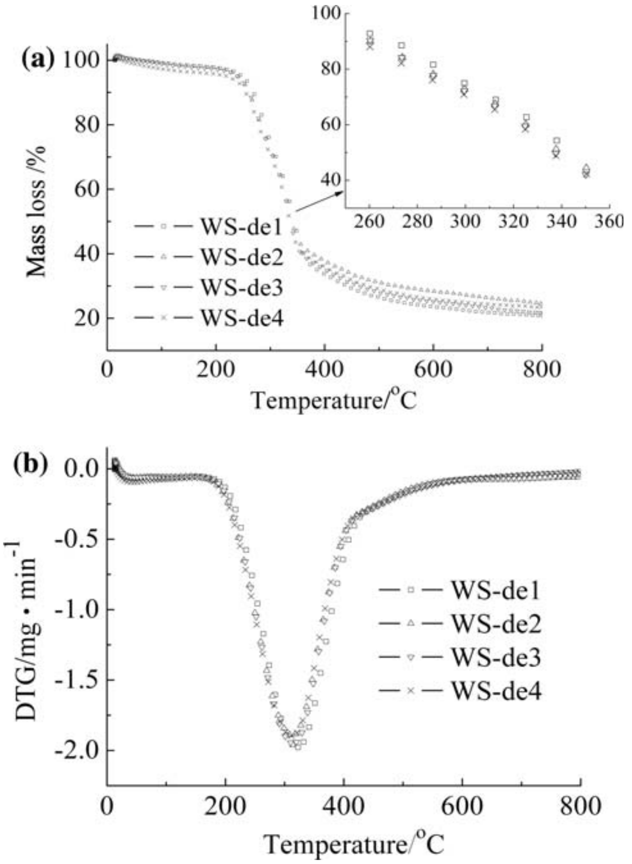

Fig. 1 TG and DTG curves for straw with different pretreatments

pretreatments are shown in Fig. 1. It can be observed that mass loss curves of straw with different pretreatments have almost the same trends, and the addition of Fe, Al or Si shifts the TG curve to a lower temperature area compared with that of WS-de1. In the presence of Si, the temperature corresponding to volatile release is the lowest. It indicates that Fe, Al or Si has catalytic actions on initial pyrolysis temperature. Char yield increases in the presence of Fe, Al or Si. The reason is that the existence of Fe, Al or Si increases resistance of interfacial heat and mass transfer, influences residual volatiles evolution accordingly.

Many investigators assumed that solid fuel pyrolysis is a first order reaction [23–28]. So the biomass pyrolysis reaction equation may simply be expressed as the following formula:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)(1-x) \tag{1}$$

where A is pre-exponential factor, E is activation energy, T is temperature, t is time, and x is mass loss fraction or pyrolysis conversion which can be calculated by

$$x = \frac{W_0 - W_\mathrm{t}}{W_0 - W_\mathrm{f}} \tag{2}$$

where W_0 is the initial mass of the test sample, W_t is the mass at time t and W_f is final mass at the end of pyrolysis. For a constant heating rate H during pyrolysis, $H = \mathrm{d}T/\mathrm{d}t$, rearranging Eq. (1) and integrating give

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}. \tag{3}$$

Since it may be shown that for most values of E and for the temperature range of the pyrolysis, the expression ln [AR/HE (1 − 2RT/E)] in Eq. (3) is essentially constant. If the left side of Eq. (3) is plotted versus 1/T, a straight line with a slope −E/R can be obtained, from which the activation energy E can be determined, as shown in Table 3.

Nitrogen species emission characteristics

Figure 2 shows the release profiles of nitrogen species with the addition of Fe, Al or Si. Compared with the dem wheat straw (WS-de1), the formation of HCN, NH_3, NO and HNCO is suppressed in higher temperature area (>390 °C) during pyrolysis. Compared with WS-de1, the nitrogen species release faster in the presence of SiO_2. The addition of SiO_2 favors the yield of nitrogen species at lower temperature (< about 350 °C), but decreases the formation of HCN, NH_3, NO and HNCO in higher temperature region. Compared with the catalytic effect of Fe or Al on the release of nitrogen species, in the presence of Si the formation of nitrogen species tends to be promoted at lower temperature, but has more obvious decrease at higher temperature. The presence of Fe, Al or Si inhibits N-conversion to NO_X precursors during pyrolysis. The addition of Si contributes to maximum reduction of nitrogen species formation.

As can be seen from Table 3, the activation energy (E) for wheat straw with the addition of Si is the smallest

Table 3 Kinetic parameters for the samples during pyrolysis

Sample	Temperature of mass loss, T (°C)	Activation energy, E (KJ mol^{-1})	Correlation coefficient, R
WS-de1	260–365	61.97	0.9942
WS-de2	245–355	58.73	0.9940
WS-de3	250–354	59.49	0.9934
WS-de4	245–350	54.14	0.9951

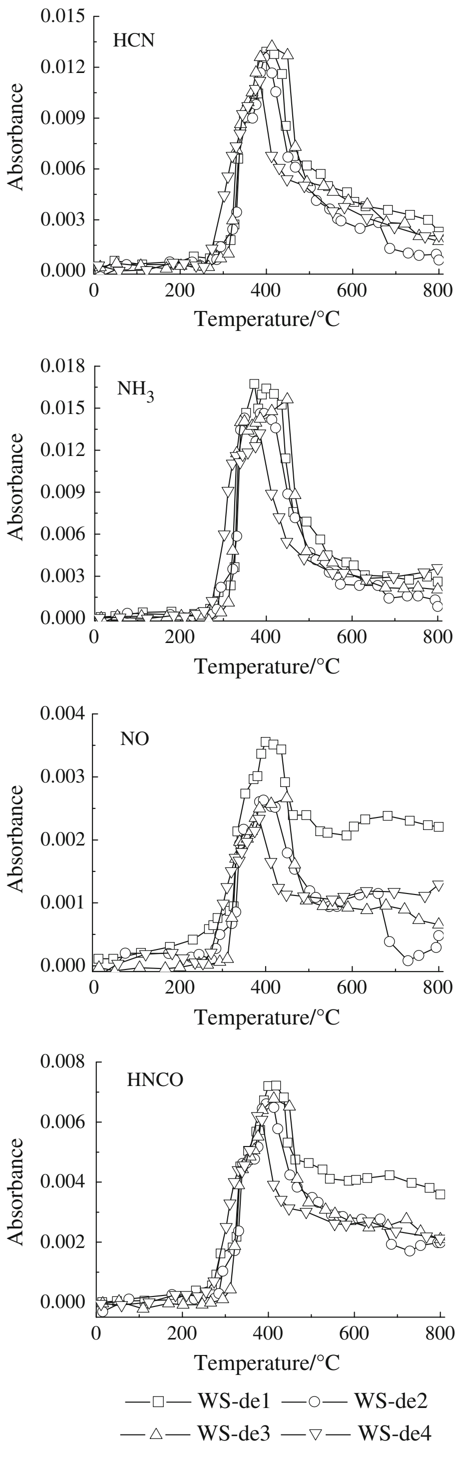

Fig. 2 Effect of excluded mineral matters on release of N-compounds during pyrolysis

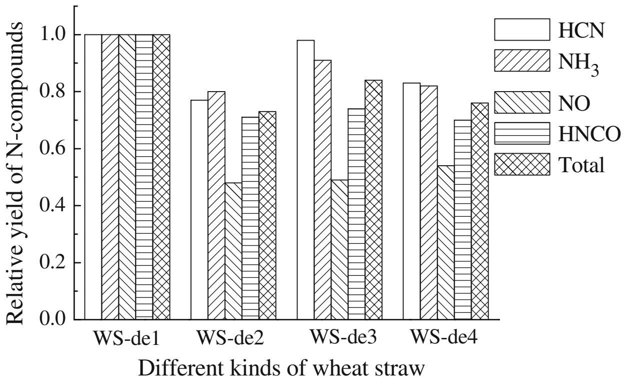

Fig. 3 Relative yield of nitrogen species from straw with different pretreatments

among the samples. Meanwhile, decreasing *E* may result from the variation in chemical structure of the wheat straw due to the addition of Si. The changed structure can be easily broken and converted to lighter species at lower temperature. It provides that thermal decomposition of wheat straw with the addition of Si is faster at lower temperature. Compared with WS-de1, nitrogen species also release faster in the presence of Fe or Al, although the trend is not obvious. It can be attributed potentially to the different catalytic effects of Fe, Al and Si.

If the yield of each of nitrogen species from WS-de1 during pyrolysis was set to be a unit, the relative values of the nitrogen species from the samples with different pretreatments were obtained and shown in Fig. 3. It is clear that the variation in the nitrogen species formation is affected by the added minerals. The added Fe, Si or Al decreases straw-N conversion to NH_3 with the sequence of Fe > Si > Al during pyrolysis. The added Fe or Si suppresses N-conversion to HCN. However, the added Al has no notable influence on HCN emission in the pyrolysis. The presence of Fe, Si or Al has almost the same effect on reduction of HNCO emission. The sum of detected values of NH_3, HCN, NO, HNCO concentration was defined as the total yields of nitrogen species formation. Figure 3 shows that the total yield of nitrogen containing species in the presence of Fe_2O_3 is the smallest.

Figure 4 shows the share of nitrogen species from pyrolysis of straw with different pretreatments. It can be concluded that NH_3 and HCN are always the main nitrogen species for all the samples. The N-conversion to NH_3 and HCN increases, but that to HNCO and NO decreases a little in the presence of Fe, Al or Si. The added Al contributes to the highest N-conversion to NH_3 and HCN, and the least to NO and HNCO. It indicates that Fe, Al or Si influences N-selectivity to HCN, NH_3 and HNCO.

HCl emission characteristics

Figure 5 shows HCl release profiles with the addition of Fe, Al or Si. The maximum HCl concentration for WS-de1 appears at 390 °C, and those in the presence of Fe, Al or Si appear at 376, 376 and 385 °C, respectively. This means that the addition of additives affects the release time when

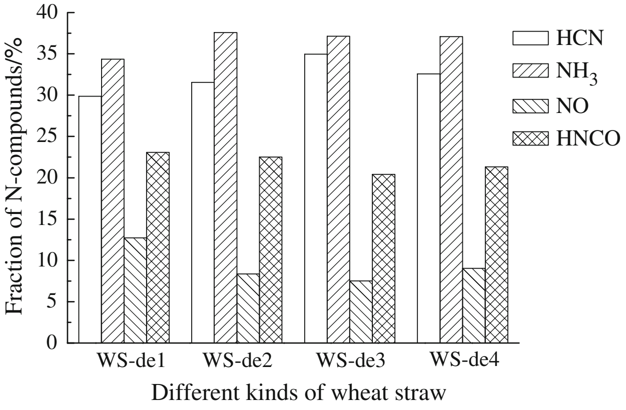

Fig. 4 Distribution of nitrogen species from straw with different pretreatments

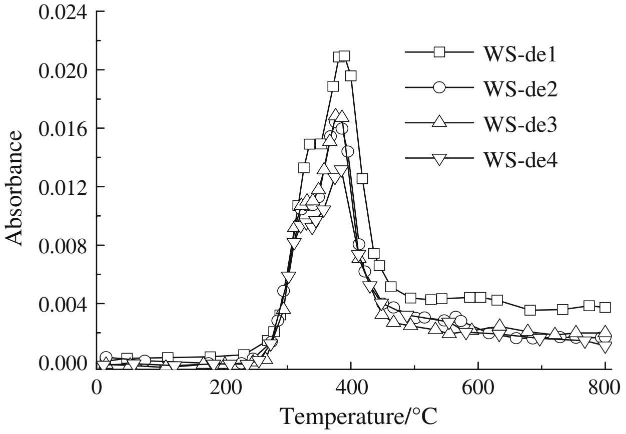

Fig. 5 HCl release for straw with different pretreatments during pyrolysis

the maximum HCl concentration appears. Compared with WS-de1, HCl emission is suppressed in the presence of Fe, Al or Si at higher temperature (>300 °C).

HCl removal reaction was a kind of gas–solid reaction. The overall process can be described by several elementary steps involving diffusion of HCl in the gas film outside the particle and in the pores inside the particle, solid diffusion of HCl through the product layer, chemical reaction, solid diffusion of product gases through the product layer, and the last diffusion of product gases film to outside [18]. The solid diffusion resistance of HCl through the product layer increases in the presence of Fe, Al or Si, which contributes to HCl removal.

If the yield of HCl from WS-de1 was set to be a unit, the relative values of HCl from the samples with different pretreatments were obtained and shown in Fig. 6. It indicates that HCl emission for WS-de4 is the smallest. In other words, the addition of SiO_2 results in the highest HCl removal rate in this study.

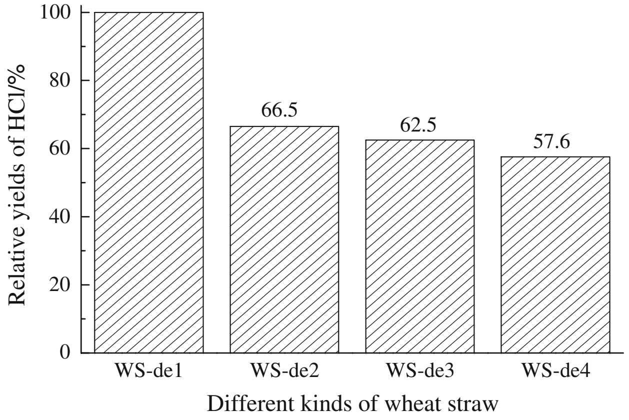

Fig. 6 Relative yields of HCl for straw with different pretreatments

Conclusions

The analytical results show that Fe, Al or Si has strong catalytic actions on straw pyrolysis. The presence of Fe, Al or Si inhibits N-conversion to NO_X precursors during pyrolysis. Moreover, the added Si contributes to maximum reduction of nitrogen species emission. Catalysts enhance the emissions of NO_X precursors at lower temperature (< about 350 °C), but inhibit the formation NO_X precursors at higher temperature during pyrolysis. The added Fe, Si or Al decreases the conversion of straw-N into NH_3 with the sequence of Fe > Si > Al during pyrolysis. The added Fe or Si suppresses N-conversion to HCN, and Al has no notable influence on HCN emission in the pyrolysis.

The catalysts influence N-selectivity to HCN, NH_3 and HNCO. The added Fe, Si or Al has almost the same effect on reduction of HNCO emission. The N-conversion to NH_3 and HCN increases, but that to HNCO and NO decreases a little in the presence of Fe, Al or Si. HCl emission is suppressed in the presence of Fe, Al or Si at higher temperature (>300 °C), and the addition of SiO_2 contributes to the highest HCl removal rate.

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