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Effect of Mixed Fe/Ca Additives on Nitrogen Transformation during Protein and Amino Acid Pyrolysis

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ABSTRACT: Considerable amounts of NO_x are generated from the thermal utilization of solid wastes. To control NO_x emission, we investigated the influence of mixed Fe/Ca additives on the generation of NO_x precursors (HCN and NH_3) during pyrolysis at 873, 1073, and 1273 K. Protein, proline, and phenylalanine were selected as model compounds to represent the primary nitrogen forms in typical solid wastes, such as biomass and sludge. According to the results, the iron effect is a remarkable property that enables the obvious reduction of NH_3. This was most likely because NH_3 was consumed by iron compounds to generate FeN_x. Iron compounds facilitated thermal cracking of heterocyclic N with the release of HCN. $Ca(OH)_2$ promoted the conversion of HCN to NH_3 and fixed HCN to form CaC_xN_y simultaneously. These intermediates (FeN_x and CaC_xN_y) play important roles in the reduction of NO_x precursors. A lower emission of NO_x precursors was observed with mixed Fe/Ca additives than with either Fe or Ca individually. This is because the generation of $Ca_2Fe_2O_5$ enhanced the tranformation of intermediates to N_2. The transformation of intermediates to N_2 was enhanced at elevated temperatures, which allows for the lowest emission of precursors (NH_3 and HCN) at 1273 K, with a higher ratio of $Ca_2Fe_2O_5$ in char.

1. INTRODUCTION

Recently, thermal utilization has become a promising treatment and disposal technology for solid wastes, owing to the valuable products generated.[1] However, it should be noted that large amounts of NO_x emitted from this process, originating from the high nitrogen content in solid wastes, cause acid rain and photochemical smog.[2−4] The content of nitrogen in sludge is as high as 6−9%,[2,5,6] and the nitrogen content in agricultural residues and aquatic plants is as high as 3−7%.[7−9] Moreover, several studies[10−12] have shown that fuel N is the main source of NO_x, especially during the combustion of N-rich solid wastes, such as biomass and sludge. Studies have shown that the N species in solid wastes mainly exist as organic N in protein and amino acids.[6,9,11,12]

It is well-accepted that fast pyrolysis plays a crucial role in the formation of NO_x.[13−15] HCN and NH_3 are the main NO_x precursors formed during pyrolysis for biomass.[10,16,17] However, owing to the diversity and complex compositions of solid wastes, it is hard to achieve a deeper understanding of the release of NO_x precursors from different kinds of solid wastes.[15,18−20]

Furthermore, nitrogen conversion varies with different nitrogen species in solid wastes during pyrolysis.[21,22] The decomposition of protein N and amine N compounds occurs easily at lower temperatures, whereas the thermal cracking of nitrile N and heterocyclic N compounds was observed at higher temperatures, ranging from 773 to 1073 K.[2] The contents of NH_3 and HCN generated during the thermal cracking of these N species were also different from each other.[23−26] The variety and interactions of amino acids influence HCN and NH_3 yields during pyrolysis to varying degrees.[25,27] Consequently, the release of NO_x precursors is associated with the thermal decomposition of nitrogen bound to protein and amino acids.

To minimize the emission of NO_x precursors, some minerals, such as calcium salts and iron salts, were applied during pyrolysis.[3,28] The total amount of NH_3 and HCN decreased from 105 to 55 μmol/g at 1173 K with the presence of metallic iron.[29] $Ca(OH)_2$ additives also suppressed NH_3 and HCN emissions from 627 to 873 K.[10] It was further indicated that the addition of iron and calcium compounds could significantly improve the conversion of biomass N to N_2 (from 8 to 31%) and decrease the amount of char N from 18 to 4%.[30] According to our previous study,[31−33] the inhibition of sludge N to NO_x precursor conversion via synergistic catalysis of Fenton−CaO was more effective than that of single Fenton or CaO catalyst. Owing to the complexity of solid waste compositions, there is thereby an urgent need but still a significant challenge to evaluate the effects of mixed Fe/Ca additives on nitrogen evolution during pyrolysis.

To gain more insight, many researchers[34,35] have used pyridine N and pyrrole N compounds as coal N models to study the transformation during pyrolysis. This method simplifies chemical components and nitrogen functionalities, which helps to pinpoint the reactivity of different nitrogen functionalities. As mentioned above, N-containing compounds in typical solid wastes largely exist as protein and amino acids. Therefore, three highly representative model compounds (protein, proline, and phenylalanine) were used in this study to gain a better understanding of the mechanism of nitrogen conversion with mixed Fe/Ca additives during pyrolysis.

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