

Catalytic upgrading of cow manure pyrolysis vapors over zeolite/carbon composites prepared from coal gasification fine slag: High quality bio-oil obtaining and mechanism investigation

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Highlights

- Different zeolite/carbon composites were prepared from coal gasification fine slag.
- Catalytic pyrolysis of cow manure over zeolite/carbon composites was evaluated.
- Relationship between catalysts structure and product selectivity was clarified.
- Mechanism of cow manure pyrolysis vapors to light aromatics was revealed.
- Model amino acids used to study the mechanism of nitrogen species transformation.

1. Introduction

Cow manure (CM) is the waste discharged from the large-scale cow breeding industry, and the environmental pollution caused by its massive accumulation is becoming increasingly prominent^[1]. Coal gasification fine slag (CGFS) is a typical industrial solid waste produced in modern coal chemical industry^[2]. The resource utilization of solid waste not only reduces the environmental pollution, but also reduces the use of fossil energy^[3]. In this study, three different types of zeolite/carbon composites were prepared using CGFS, including Y-type zeolite/carbon, Beta zeolite/carbon and ZSM-5 zeolite/carbon. The composition and distribution of products from the catalytic upgrading of CM pyrolysis vapors over three kinds of composites were studied, and the correlation between the physicochemical structures such as the pore structure and acid sites of the catalyst and the selectivity of the products was investigated. Further, the model compounds were selected for catalytic pyrolysis to reveal the mechanism of catalytic conversion of CM pyrolysis volatiles into light aromatic hydrocarbons and the migration characteristic of nitrogen-containing species. The results can provide reference and theoretical guidance for the comprehensive utilization of industrial solid waste and organic solid waste and the development of low-carbon green industry.

2. Methods

Firstly, acid leaching pretreatment was performed on CGFS to remove impurity elements such as iron, calcium, and sodium, and the silicon-aluminum ratio of acid leaching CGFS was adjusted by changing the acid leaching temperature. Then, different types of zeolite/carbon composite catalysts were prepared by hydrothermal crystallization method.

The crystalline phases of CGFS and the prepared zeolite/carbon composites were analyzed by XRD. The functional groups of CGFS and the skeleton structure information of the synthesized zeolite/carbon composites were analyzed by FT-IR. The weight loss process of zeolite/carbon at elevated temperature was analyzed by TG. The surface morphology of the samples was observed by SEM. The acid sites of the samples were analyzed by NH₃-TPD.

The direct pyrolysis and catalytic pyrolysis of CM were carried out on a pyrolysis probe coupled with gas chromatography-mass spectrometry (Py-GC/MS). For the direct pyrolysis of CM, 0.6 mg of sample was weighed and placed in a quartz tube. The bottom of the quartz tube is supported by a quartz rod and filled with quartz wool to prevent sample loss. The pyrolysis temperature was 500°C, 600°C, 700°C and 800°C, respectively, and the heating rate was 100°C/s.

3. Results and discussion

Figure 1 shows the product composition and distribution of CM direct pyrolysis and catalytic pyrolysis over different types of zeolite/carbon composites. Figure 1(a) illustrates the product distribution of CM direct pyrolysis at different temperatures. The main products of direct pyrolysis bio-oil of CM are phenolic compounds, oxygenated compounds (OCs) such as alcohols, ketones, ethers, esters, and nitrogen-containing heteroatom compounds (NCs), which are mainly a series of complex dehydration, dehydrogenation, decomposition, condensation during the pyrolysis of cellulose, hemicellulose, lignin and crude protein abundant in CM. It also contains a small amount of monocyclic aromatic hydrocarbons (MAHs) and aliphatic compounds (AHs). Figure 1(b), (c) and (d) show the product distribution of the volatiles from the pyrolysis of CM catalyzed by different amounts of ZSM-5/C, Beta/C, and Y-type/C composites, respectively. Evidently, the three catalysts can significantly improve the yield of MAHs, and with the increase of catalyst addition, the yield of MAHs continues to increase. When the amount of ZSM-5/C and Beta/C catalysts is 1.0 mg, the yield of MAHs is almost four times that of direct pyrolysis, and when 1.0 mg of Y-type/C catalyst is added, the yield of MAHs also increases by two times, which may be the acidic sites provided by the composite catalyst, and these were conducive to the occurrence of aromatization reaction, thereby promoting the formation of aromatic hydrocarbons. Moreover, under the catalysis of ZSM-5/C, Beta/C, and Y-type/C composite catalysts, the yield of polycyclic aromatic hydrocarbons (PAHs) mainly composed of naphthalene and methylnaphthalene increased significantly, and it is positively correlated with the amount of catalyst input. Among them, Beta/C catalyst has the greatest improvement on the yield of naphthalene, which may be related to the physicochemical structure of the catalyst, such as acid sites and pore size distribution. The relatively large pore size of the Beta zeolite is conducive to the formation of aromatic hydrocarbons of large molecular weight such as naphthalene series, while the smaller pore size of ZSM-5 zeolite has selective catalysis, which is more conducive to the formation of MAHs. In contrast, the yields of phenol, AHs, OCs and NCs decreased significantly under the catalysis of three zeolite/carbon composites. Among them, Y-type/C has the most obvious inhibitory effect on the yields of phenol, AHs, OCs and NCs. This shows that the three catalysts can significantly improve the quality of CM pyrolysis bio-oil.

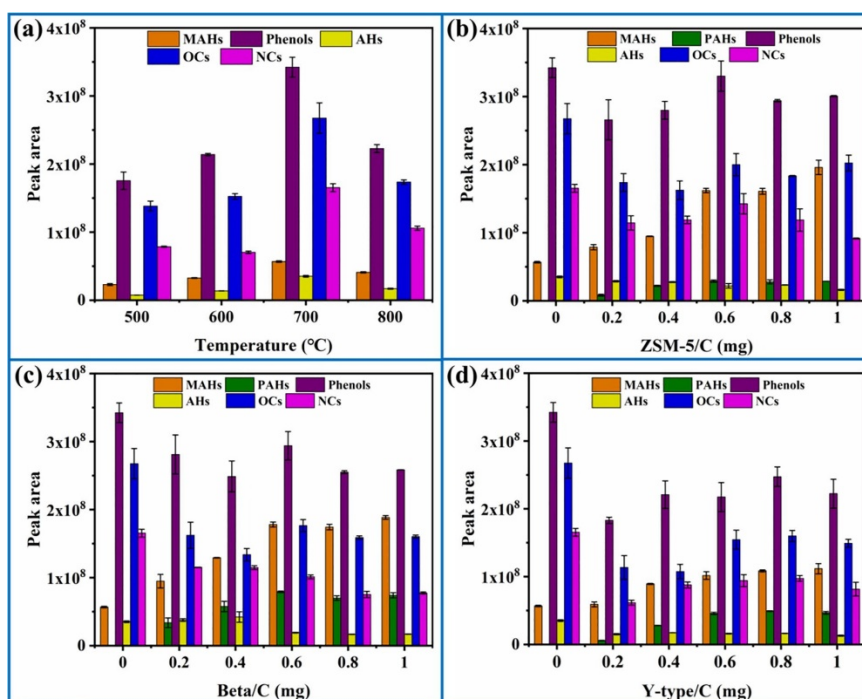


Figure 1. (a) The distribution of products from direct pyrolysis of CM at different temperatures, distribution of products from catalytic pyrolysis of CM over different types of zeolite/carbon composites (b) ZSM-5/C, (c) Beta/C, (d) Y-type/C.

4. Conclusions

The results show that three different types of zeolite/carbon composites have catalytic effects on the pyrolysis vapors of CM, but have different regulatory effects on the composition and distribution of the products. Among them, ZSM-5/C and Beta/C composites have better catalytic effect due to their

suitable acidic sites. After catalytic upgrading, the yield of monocyclic aromatic hydrocarbons can reach 4 times of that of direct pyrolysis, and the yield of monocyclic aromatic hydrocarbons can be increased to 2 times of that of direct pyrolysis after Y type/C catalysis. The smaller pore size of ZSM-5 has shape selective catalysis, which is more conducive to the formation of monocyclic aromatic hydrocarbons. The relatively larger pore size of Beta will promote the formation of macromolecular aromatic hydrocarbons, such as naphthalene series. These three composites can reduce the formation of oxygen and nitrogen compounds in the pyrolysis products and improve the quality of bio-oil. Furthermore, the catalytic pyrolysis experiment of model compounds revealed the possible catalytic conversion mechanism.

References

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Keywords

Pyrolysis; Light aromatics hydrocarbons; Zeolite/carbon composites; Cow manure; Coal gasification fine slag