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Effects of alkali and alkaline earth metals on the formation of light aromatic hydrocarbons during coal pyrolysis

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ABSTRACT

Light aromatic hydrocarbons from coal pyrolysis such as benzene, toluene, xylene, and naphthalene have been found wide applications as industrial raw materials. The alkali and alkaline earth metals (AAEMs) are of considerable effect on the yield and distribution of coal tar during pyrolysis. In this study, the yield and distribution of the pyrolysis products of three raw coals with different ranks, demineralized coals prepared by acid washing, and metal-loaded coals were investigated using pyrolysis–gas chromatograph/mass spectrometer (Py–GC/MS). The results show that the yields of benzene, xylene, toluene, and naphthalene are significantly different before and after acid washing, and the generation of light aromatic hydrocarbons has an obvious dependency on AAEMs in coal. AAEMs have good catalytic activity on the decomposition of phenols and condensed aromatics to light aromatic hydrocarbons.

1. Introduction

Light aromatic hydrocarbons such as benzene, toluene, xylene and naphthalene (BTXN) are high value added chemicals that have been found a variety of applications as industrial raw materials. Coal pyrolysis provides an alternative source to petrochemical industry for the production of these chemicals [1]. The alkali and alkaline earth metallic species (AAEMs) in coal can have a considerable effect on the pyrolysis behavior and coal tar distribution [2–5]. For instance, Öztaş and Yürüm [2] showed that K, Fe and Mg metals had catalytic effects on the conversion rate of pyrolysis. Sathe et al. [6] also showed that AAEMs have important influence on the distribution of pyrolysis products, especially at high pressures. CaO exhibited good catalytic activity in catalytic cracking of coal tar, volatile organic compound as 'tar' model compounds, and some polymer mixture [7–9]. The yield of the liquid products was increased by 4–6%, whereas the yield of the wax residue was reduced by 2% during pyrolysis of a mixture consisting of polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) using calcium ($CaCO_3$ and Ca-C composite) based catalysts [7]. Furthermore, the yields of tar and volatile matters released from pyrolysis of demineralized coals were higher than that of raw coals [10,11]. Thus, it is possible that the presence of monovalent and divalent cations in coal can result in the decrease in tar yield due to their cross linking effects [12–15]. Both monovalent and divalent cations can convert tar into char and tighten char structure, thus making it difficult for the heavy tar molecules to escape. They may also change the constituents of the resulting tars during coal pyrolysis.

Despite extensive studies have been focused on the effects of AAEMs on the pyrolysis behavior, char yield, and tar yield, little is known about the roles of AAEMs in the formation and distribution of light aromatic hydrocarbons during coal pyrolysis. To better understand the roles of AAEMs during coal pyrolysis, the yield and distribution of the pyrolysis products of three raw coals with different ranks (lignite, subbituminous, and bituminous coal), demineralized coals prepared by HCl/HF acid washing, and metal-loaded coals were investigated and compared in this study.

2. Experimental

2.1. Coal samples

Three raw coals with different ranks (lignite, subbituminous, and bituminous coal) were used in this study, which was denoted as coal A, B, and C, respectively. These coals were ground and sieved to a particle size of 0.15–0.30 mm, and their proximate and ultimate analyses were shown in Table 1. They were subjected to HCl/HF washing as described previously [16] to remove metal elements, and their demineralized coals were denoted as coal DA, DB, and DC, respectively. The contents of metals (e.g., K, Na, Ca, and Mg) in

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Table 1
Proximate and ultimate analyses of coal samples.

Sample	Proximate analysis wt/%			Ultimate analysis wt/%, daf				
	M_{ad}	A_{ad}	V_{daf}	C	H	O[a]	N	S
Coal A	11.7	15.3	46.5	69.0	4.3	24.7	1.2	0.7
Coal B	14.8	3.0	33.8	75.9	3.0	19.9	0.7	0.5
Coal C	0.5	9.0	22.9	86.1	4.7	7.1	1.7	0.4

Note: ad: air dry; daf: dry and ash free basis.
[a] By difference.

each coal were measured by atomic absorption spectroscopy (AAS) according to Chinese Standard GB-T1574. Metal-loaded coals were prepared by impregnating demineralized coal into the solutions of K_2CO_3, Na_2CO_3, $Ca(CH_3COO)_2$, and $Mg(NO_3)_2$ according to the method reported elsewhere [17], which were denoted as K-, Na-, Ca-, and Mg-coal, respectively.

2.2. Pyrolysis experiments

Coal samples were placed in the quartz pyrolysis tubes equipped with quartz filler rods and sealed at each side using quartz wool to avoid possible leakage, and then heated by a 2–3 mm diameter platinum filament in a Chemical Data Systems (CDS) Pyro-probe 5250. It was noteworthy that different amounts of raw coal, demineralized coal, and metal-loaded coal samples were used to ensure the same content of organic components. The samples were pyrolyzed at different temperatures (500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C) at a heating rate of 10,000 °C/s and a residence time of 15 s, and then the pyrolysis products were detected by GC/MS on-line. Helium (99.999%) was used as the carrier gas to purge the pyrolysis products to GC.

2.3. Gas chromatograph/mass spectrometer (GC/MS) analysis

The pyrolysis products of raw coal, demineralized coal, and metal-loaded coal samples entered GC column through a transfer line, where they were separated and detected by MS. The GC/MS instrument consisted of a Focus gas chromatograph and a Dual Stage Quadrupole-II (DSQ) mass spectrometer (Thermo Fisher, USA). Helium was used as the GC carrier gas at a flow rate of 1 mL/min and a split ratio of 1:50. DB-5MS capillary column was used as the GC column. The GC oven temperature was held at 40 °C for 4 min, then heated to 70 °C at a rate of 4 °C/min and held for 2 min, then heated to 200 °C at a rate of 10 °C/min and held for 3 min, and finally heated to 300 °C at a rate of 4 °C/min and held for 5 min. MS was operated in electron ionization (EI) mode at 70 eV from 50 to 600 m/z with a speed of 3000 amu/s. The chromatographic peaks of light aromatic hydrocarbons (benzene, toluene, xylene (m/p-xylene and o-xylene), and naphthalene) were identified using the chemical standards and National Institute of Standards and Technology (NIST) MS library. The experiments were repeated at least four times to ensure that the results were reproducible. Experiments results are expressed as average value.

3. Results and discussion

3.1. Effects of AAEMs on BTXN yield

The release amount of BTXN from three coal pyrolysis is low before 500 °C, and there were no obvious differences in BTXN yields before and after acid washing, as shown in Fig. 1. It is probably because the low degree of thermal decomposition of coal structure at this temperature ranges. The temperature interval for coal tar release is found between 600 and 700 °C when coal samples are heated at 1000 °C/s, which is quite different with slow heating [18].

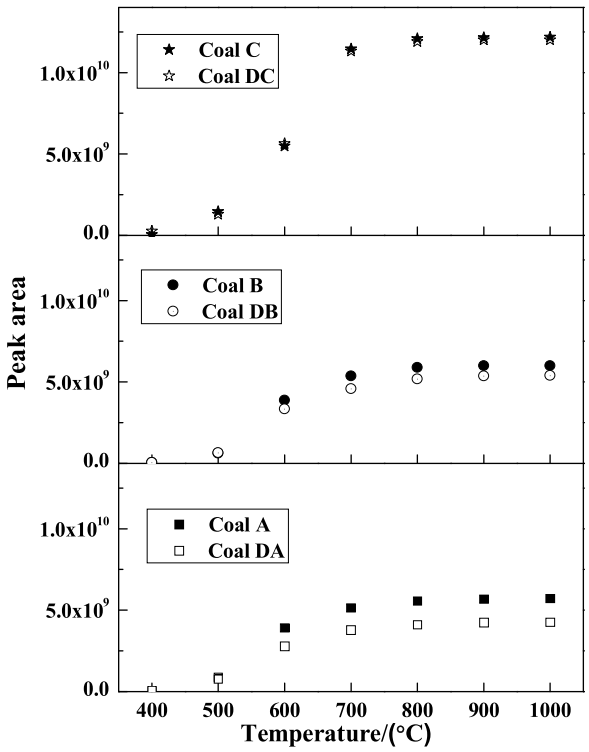

Fig. 1. Total yield of BTXN during pyrolysis of raw and demineralized coals.

Table 2
AAEMs contents in coals (%, db).

	Coal A	Coal B	Coal C	Coal DA	Coal DB	Coal DC
K	0.37	0.02	0.05	0.01	0.01	0
Na	1.27	0.17	0.30	0.08	0.05	0.03
Ca	0.04	1.08	0	0.01	0.01	0
Mg	0.42	0.21	0.02	0.04	0.01	0.01

Therefore, AAEMs in coal have no obvious effect on BTXN release before 500 °C.

Total amount of BTXN generated from raw coals and their demineralized coals pyrolysis shows different trends after 600 °C. The BTXN yields of coal A and coal B are higher than that of coal DA and coal DB, respectively. The difference in BTXN yields of coals before and after acid washing become more obvious. For example, BTXN yields of coal A and coal B are about 1.5 and 1.2 times than that of coal DA and coal DB at 700 °C, respectively. Extensive depolymerization of coal structure takes place between 500 and 800 °C, and BTXN yields are observed to rise rapidly. It seems that AAEMs play a critical role in the formation of BTXN at this temperature range. The similar phenomenon is also investigated in temperature range of 800–1000 °C. But BTXN yields are rarely changed since polycondensation of coal structure is the main reaction after 800 °C. Thus, AAEMs in coal A and coal B can promote the formation of light aromatic hydrocarbons during coal pyrolysis. However, the BTXN yield of coal C is almost the same as that of coal DC in temperature range of 400–1000 °C. So the effect of AAEMs in coal on BTXN formation is obviously different during three coals pyrolysis.

The metals in three raw coals and their acid washing residues were determined by AAS and shown in Table 2. The total contents of K, Na, Ca, and Mg metal in three demineralized coals are less than 0.10%, so the effect of AAEMs on the BTXN formation during pyrolysis can be ignored. The total content of K, Na, Ca, and Mg metal in coal A is as high as 2.10%, in which Na metal account for 1.27%; while the total content of AAEMs is about 1.48% in coal B, which is mainly composed of Ca; and it is merely 0.37% in coal