Full Length Article

Effects of low molecular compounds in coal on the catalytic upgrading of gaseous tar

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ABSTRACT

The main purpose of this study was to investigate the effects of low molecular compounds in coal on the formation of benzene, toluene, xylene and naphthalene (BTXN) in the catalytic upgrading of tar from coal pyrolysis by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Low molecular compounds were extracted from mineral-free lignite (Coal DA) and bituminous coal (Coal DB), and then the gaseous tars from the pyrolysis of residual coal (Coal DAR and Coal DBR), extraction solution (AE and BE) and mineral-free coal were subjected to catalytic cracking using USY zeolite as catalyst. The results show that the total amount of BTXN in the extraction solution and residual coal is 27% and 4.8% lower than that in Coal DA and Coal DB during catalytic upgrading of gaseous tars, respectively. The presence of low molecular compounds can result in a significant increase in the BTXN amount after catalytic reforming. The extraction solution in Coal DA are predominantly aliphatic compounds (72.7%) and Oxygen-containing aromatics (21.9%), whereas that in Coal DB is naphthalene series (33.1%), condensed aromatics (29.4%), and aliphatic compounds (23.5%). Phenols and condensed aromatics in low molecular compounds can be cracked into BTXN under the catalysis of USY zeolite. More heavy aromatics are cracked to light arene instead of polycondensation in the presence of aliphatic compounds.

1. Introduction

Catalytic upgrading of tar from coal pyrolysis has become an effective approach to produce high-quality coal tar and chemicals. The use of catalysts such as ZSM-5 zeolite [1–3], Y zeolite [4–5] and carbon-based catalysts [6] could result in a substantial increase in the yield of light oil, especially those light arenes such as benzene, toluene, xylene and naphthalene (hereinafter collectively referred to as BTXN). For example, Cao et al. [3] investigate the catalytic fast pyrolysis of lignite vapors using metal-loaded HZSM-5 as the catalyst, and the results showed that the aromatics content in tar was up to 94.2% (area%) under the action of metal and acid sites. Thus, catalytic upgrading of tar from coal pyrolysis contributes significantly to conversion and utilization of coal resources.

Coal is composed mainly of organic macromolecular skeleton in dispersed form with a variety of free low molecular compounds attached to the main structure of coal through hydrogen bonds or van der waals force [7]. These low molecular compounds are derived from components of coal-forming plants, such as resins, tree wax, terpenes and sterols. The compositions of low molecular compounds are very complex and vary with coal rank, and the molecular weights are about

500 or less [8]. Therefore, low molecular compounds appear to have higher thermal decomposition rate and lower apparent activation energy than aromatic skeleton structure in coal [9], and their chemical properties also differ significantly.

Previous studies have shown that low molecular compounds in coal have an effect on coal pyrolysis and tar distribution [10–11]. Zou et al. [10] investigated the products distributions in lignite and their extracted residual coal using tetrahydrofuran as solvent, and the results showed that the total tar yield of residual coal was lower than that of raw coal. The aromaticity of tar generated from residual coal was higher than that of raw coal. He et al. [11] also reported that benzene and toluene were mainly derived from thermal cracking of coal macromolecular structures, but low molecular compounds could promote the formation of light arene. Thus, low molecular compounds have an effect on tar yield and composition, and consequently the formation of light arene during coal pyrolysis. However, their role in the catalytic reforming of tar from coal pyrolysis remains largely unknown.

In this study, low molecular compounds were extracted from coal using pyridine as the solvent, and the gaseous tar from the pyrolysis of extract solutions, residual coal, and mineral-free coal was subjected to catalytic cracking using USY zeolite. Then, the distribution of BTXN

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Table 1
Proximate and ultimate analyses (wt%) of coal samples.

Sample	Proximate analysis			Ultimate analysis (daf)				
	M_{ad}	A_{ad}	V_{daf}	C	H	O^*	N	S
Coal A	11.7	15.3	46.5	69.0	4.3	24.7	1.2	0.7
Coal B	0.5	9.0	22.9	86.1	4.7	7.1	1.7	0.4
Coal DA	5.7	0.2	44.6	69.5	4.5	24.2	1.2	0.6
Coal DB	0.6	0.1	19.8	87.4	4.5	6.5	1.7	0.5

Note: ad: air dried; daf: dry-and-ash-free. *by difference.

before and after catalytic cracking was compared to assess the effects of low molecular compounds in coal on the catalytic upgrading of coal tar.

2. Experimental

2.1. Samples

Two coals with different ranks were used in this study, including lignite (Coal A) from Xilin Gol League in Inner Mongolia Autonomous Region of China, bituminous coal (Coal B) from Hexi Coal Mine in Shanxi province of China. All samples were crushed to 0.15–0.30 mm, and then kept in a dryer for subsequent experiments. To minimize the effects of minerals in coal, minerals were removed from raw coal using HCl/HF as described previously [12], and the mineral-free Coal A and Coal B were denoted as Coal DA and Coal DB, respectively. Table 1 shows the proximate and ultimate analyses of coals. USY zeolite was purchased from Nankai Catalyst Company (Tianjin, China).

2.2. Extraction experiments

Pyridine extraction was performed using an automatic Soxhlet extractor (Gerhardt Soxtherm macro 414) until the color of the extraction solution turned into light yellow. 2.0 g coal sample was added. The extraction solution was evaporated to a volume of 5 mL using a rotary evaporator, which was denoted as AE and BE, respectively. The residual coal after pyridine extraction was dried in a vacuum oven at 80 °C for 3 h and then its weight was measured. The residual coal after pyridine extraction was denoted as Coal DAR and Coal DBR, respectively. The extract yield (wt.%) of Coal DA and Coal DB was 23.7% and 7.2%, respectively, which was calculated using the following formula:

$$wt\% = \frac{100 \times (m_1 - m_2)}{m \times (100 - M_{ad} - A_{ad})} \times 100\%$$

where m_1 and m_2 (g) were the total weight of the coal sample and filter before and after extraction, and m (g) was the weight of coal sample, respectively.

2.3. Py-GC/MS experiment

Coal pyrolysis was carried out using a CDS Pyroprobe 5250 pyrolyser. 1 mg of coal samples were added into a quartz tube filled with quartz chips and supported by quartz wool to perform the pyrolysis experiments. In the catalytic cracking experiments, 1 mg of mineral-free coal (Coal DA or Coal DB) and 0.6 mg of catalysts were added into the quartz tube and separated by quartz wool, heated to 800 °C at a heating rate of 10 °C/ms and then maintained at that temperature for 15 s. Later, 0.76 mg of Coal DAR or 0.93 mg of Coal DBR was selected according to the extract yield of each coal. The amount of BTXN from pyridine extraction solutions with a volume of 1 μL in the presence of catalyst was also detected by Py-GC/MS under the same conditions as that of mineral-free coal. High-purity Helium (99.999%) was used as the carrier gas to purge the pyrolysis products to GC through the transfer line heated at 275 °C. The amount of BTXN (n) from pyridine extraction solutions in 1 mg coal was calculated using the following

formula:

$$n = \frac{(n_0 \times 5000) \times 1mg}{2g}$$

where n_0 was the amount of BTXN from pyridine extraction solutions (1 μL) in the presence of catalyst, 2 g and 1 mg was the weight of the coal sample in the extraction experiment and the Py-GC/MS experiment, respectively.

The pyrolysis products were analyzed using GC/MS (Focus GC-DSQ II, Thermo Scientific, USA). A DB-5MS capillary column was used as the GC column. The carrier gas was Helium at a flow rate of 1 mL/min and a split ratio of 70: 1. The inlet temperature was 250 °C, and the GC column temperature was programmed as follows: initially held at 40 °C for 4 min, increased to 70 °C at a rate of 3 °C/min and held at this temperature for 2 min, then increased to 200 °C at a rate of 10 °C/min and held at this temperature for 3 min, and finally increased to 300 °C at a rate of 4 °C/min and held at this temperature for 5 min. MS measurements were performed with electron ionization at a voltage of 70 eV and an ion source temperature of 250 °C. The scanning rate was 3000 amu/s, and the m/z scanning range was set to 50–650. The chromatographic peaks were identified using the NIST MS library (US National Institute of Standards and Technology) and chemical standards, and quantified by an external standard method. All experiments were replicated three times, and the amount was expressed based on the dry and ash-free coal samples. In the GC/MS analysis of pyridine extraction solution (low molecular compounds), splitless injection was used with an injection volume of 1 μL.

2.4. CP/MAS ^{13}C NMR analysis

Cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR was performed on a 500 MHz Bruker Avance III spectrometer. Dried coal samples were added into a 4 mm ZrO_2 sample tube. The resonance frequency was 500 MHz. Total spinning sideband suppression (TOSS) was used at a spinning speed of 5 kHz, a polarization contact time of 3 s, and a recycle delay time of 1 s. All ^{13}C chemical shifts were measured based on the glycine, whose carbonyl chemical shift was at 176.03 ppm. The CP/MAS ^{13}C NMR spectra of coals were obtained.

2.5. Characterization of zeolite catalysts

The textural properties of USY zeolites were measured using a Jwbk122w micropore analyzer (Beijing Jwgb Sci. & Tech. Co., Ltd., China). The surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation, and the pore volume and average pore diameter were calculated using the Barrett–Joyner–Halenda (BJH) method. The acidity on USY zeolites was determined by temperature programmed desorption of ammonia (NH_3-TPD). The experimental procedures can be seen in the literature [5].

3. Results and discussions

3.1. Properties of USY zeolite

The surface area and pore volume of USY zeolite is 637 m^2/g and 0.1 cm^3/g, respectively. The average pore diameter is 2.48 nm. The cation type of USY zeolite used in this study is the H form with a Si/Al ratio of about 7. Fig. 1 shows that there are two distinct peaks in the NH_3-TPD spectra of USY zeolite, indicating the presence of both weak and strong acid sites, respectively. Therefore, USY zeolites with a large number of weak and strong acid sites will show good performance on the catalytic upgrading of gaseous tars.