Pyrolysis of Yulin coal over ZSM-22 supported catalysts for upgrading coal tar in fixed bed reactor

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ABSTRACT

In the present study, catalytic pyrolysis of Yulin coal (YLC) using ZSM-22-supported catalysts was performed in a fixed-bed reactor and the resulting liquid products were determined with gas chromatography/mass spectrometer (GC/MS). The zeolite ZSM-22 and ZSM-22-supported CoO_X, MoO_3 and CoO_X-MoO_3 catalysts were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), transmission electron microscope (TEM), scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDS) and temperature-programmed desorption of NH_3 (NH_3-TPD). The results showed that ZSM-22 and its metal oxides/ZSM-22 (MOs/ZSM-22) catalysts result in a higher tar yield, whereas lower char yield is produced. More importantly, the yield and distribution of tar could be controlled by tuning the type of acid sites of the catalysts. All catalysts significantly selectively improved the relative contents of aliphatics, arenes and phenols, whereas inhibited those of alcohols and nitrogen-containing compounds. Among those catalysts, MoO_3/ZSM-22 was found to be more effective in producing phenols, and CoO_X/ZSM-22 showed better performance in upgrading tar quality in terms of high selectivity for aliphatics (49.50%) and arenes (21.01%), while CoO_X-MoO_3/ZSM-22 favored to produce kerosene (13.75%).

1. Introduction

Coal, which contains complex organic compositions having different molecular weights and structures, is a major energy source accounting for ca. 70% of primary energy demands in China [1]. However, thermoelectricity production from coal leads to CO_2 emissions and climate deterioration. Driven by the increasing environmental concerns, Chinese government proposed that carbon emission would be cut by 40–45% in 2020 [2]. Therefore, extensive technical efforts have been focused on converting coal into useful liquid fuels through an alternative process, such as liquefaction [3], gasification [4] and pyrolysis [5].

Pyrolysis, as a promising conversion technology for reducing environmental impacts, has been extensively studied for producing char, tar and fuel gases [6–9]. Tar is considered as a partial alternative to feedstock of transportation fuels [10], while char can be used to produce activated carbon [11,12]. Comprehensive understanding the mechanism of coal pyrolysis is vital in obtaining higher tar yield. Extensive researches have been devoted to clarify the effects of pyrolysis conditions, such as the temperature, pressure, residence time, atmosphere, heating rate, etc. [13–17], on products yields and distribution. However, due to the heterogeneity and complexity of coal structure as well as the limitation of the pyrolysis process involved, it is still a challenge to convert heavy oil into light tar and gases merely by tuning reaction conditions of pyrolysis processing.

Catalytic pyrolysis, which involves the pyrolysis of coal in the presence of catalyst, can efficiently manipulate pyrolysis products distribution and promote the yields of high value-added liquid and gaseous products, such as aromatics and aliphatics. Extensive studies have been conducted to optimize pyrolysis products from coal by applying various of minerals [18], alkali [19] and alkaline-earth metals [20], metal oxides [21], carbon materials [22], molecular sieves [23] and supported transition or noble metal [24] as catalysts. Minerals could crack the side chains of catechol to generate phenols during the pyrolysis of Ximeng lignite [25]. The iron-based catalysts, including Fe_2O_3, Fe_2S_3, FeS, and $FeSO_4$, decreased the tar yield in the pyrolysis of Shendong long-flame coal, while increased the formation of the n-hexane soluble compounds [26]. Activated carbon (AC) catalyst possessing high surface area and large pore volume is beneficial for converting heavy fraction into light tar [27]. USY zeolite was found to be effective in upgrading tar by increasing the amount of light arenes [28]. Meanwhile, Han et al. [29] indicated that transition metal incorporated char catalysts (Co-char, Ni-char, Cu-char, Zn-char) favored light tar and non-condensable gases due to the secondary reaction resulting in decrease of

heavy tar. The similar phenomenon was also found in the presence of nickel incorporated zeolite, non-condensable gases were reduced, whereas the light pyrolysis oil was promoted [30]. Moreover, HZSM-5 and Mo/HZSM-5 could increase the yield of BTEXN (benzene, toluene, ethylbenzene, xylene, naphthalene) in Pingshuo coal pyrolysis [31]. NaX promoted the generating of CO, CH_4 and aromatics during the pyrolysis of Huang Tu Miao coal [32].

GC/MS has been extensively applied to characterize the structural features and compositions of the volatiles in tar, including monocyclic and polycyclic aromatics, aliphatics, phenols, alcohols and nitrogen-containing compounds [33]. The light volatiles produced from low rank coal pyrolysis consisted of 13% monocyclic aromatics, 7% polycyclic aromatics, 40% phenols, 33% aliphatics and 4% oxygen-containing compounds [34]. Monocyclic aromatics, such as BTX consisting of benzene, toluene and xylene were the favorable products under hydrogen atmosphere, because hydrogen induced the devolatilization of lignite, resulting in more light hydrocarbons [35]. The low rank coal generated more phenols than higher rank coal, while PAHs (polycyclic aromatic hydrocarbons) emission increased with coal rank [36,37].

The current research reports the catalytic pyrolysis of YLC to determine the effects of ZSM-22 and MOs/ZSM-22 catalysts on the yields of pyrolysis products (char, tar, gas) and the distribution of tar. TGA was implemented to determine the optimum reaction temperature for the fixed-bed reactor experiment. The tar produced from noncatalytic and catalytic pyrolysis was determined by GC/MS. For upgrading coal tar quality during YLC pyrolysis, ZSM-22-supported metal oxides catalysts were prepared and fully characterized. Furthermore, their catalytic performances were detailed investigated to understand the possible relationship between the physico-chemical nature and activities of the catalysts.

2. Experimental

2.1. Coal sample

The coal sample used in this study was collected from Yulin, Shaanxi Provinces, and is denoted as YLC for convenience. The proximate and ultimate analyses of YLC were shown in Table 1. Prior to each pyrolysis experiments, YLC was grounded and sieved to obtain a particle size less than 160 meshes, then dried at 80 °C for 12 h.

2.2. Catalyst preparation

ZSM-22 (Nanjing Boyun Chemical Technology Co. Ltd) zeolite was calcined at 550 °C for 6 h. The 3% MOs/ZSM-22 catalysts were prepared by the ion-exchange method. A certain amount of ZSM-22 was added into $Co(NO_3)_2 \cdot 6H_2O$ or/and $(NH_4)_6Mo_7O_2 \cdot 4H_2O$ solution and stirred at 40 °C for 24 h. The suspension was filtered, washed several times with deionized water, and then the precipitate was dried at 80 °C for 8 h, followed by calcination in air at 500 °C for 4 h. The obtained samples were denoted as CoO_X/ZSM-22, MoO_3/ZSM-22 and CoO_X-MoO_3/ZSM-22.

2.3. Catalyst characterization

XRD analysis was performed on a Rigaku D/220-PC diffractometer with a Cu Kradiation operated at 40 kV and 30 mA with scanning rate of 5 °C min^{-1} at 2θ from 5 to 60°.

BET surface areas (S_{BET}), BJH pore diameter (D_{BJH}) and total pore volume (V_{total}) were determined from nitrogen adsorption-desorption isotherms using a QUADRASORB SI Quantachrome USA analyzer.

The surface morphology of catalysts was obtained by SEM (Carl Zeiss SIGMA) equipped with an EDS system for full-scale elemental analysis.

TEM analysis was performed on a JEOLJEM-2011 operated at a voltage of 120 kV. A small amount of catalyst was ultrasonically suspended in ethanol, and then the sample was prepared by dropping the dispersed suspensions onto a carbon-coated copper grid.

Temperature-programmed desorption of NH_3 (NH_3-TPD) was performed with a Quantachrome CHEMBET-3000 instrument. 200 mg sample were pretreated in a N_2 stream (99.99%, 30 mL min^{-1}) at 500 °C for 1 h. After being cooled down to 50 °C, NH_3 was injected in a pulsed manner until saturation. The NH_3-TPD analysis was carried out by heating the samples from 50 to 600 °C at a heating rate of 10 °C min^{-1}.

2.4. Pyrolysis experiments in the fixed-bed reactor

The pyrolysis of YLC with and without catalyst was carried out in a micro scale and vertical fixed-bed reactor at 450 °C for 30 min. H_2/N_2 (5%) was fed at the top of quartz tube, with a constant total flow rate of 100 mL min^{-1}. The experiments conducted under 5% catalyst/coal ratio. The liquid product (tar) was collected in ethanol cooled trap at −30 °C. The tar and the residue (char) were weighed for calculation. In order to establish mass balance, the gas yield was determined by difference.

2.5. GC/MS analysis

The compositions of tar were analyzed by Shimadzu GCMS-QP 2010 plus instrument with a capillary column (Rtx–5 ms, 30 m × 0.25 mm × 0.25 μm). The mass spectrometer was operated in electron impact mode (70 eV) and the ion source temperature was set at 230 °C. The GC oven was programmed to start at 60 °C (held for 1 min), heated up to 90 °C (held for 1 min) at a rate of 3 °C min^{-1}, increased to 170 °C (held for 1 min), then to 300 °C (held for 8 min). Both the GC injector and the GC/MS interface temperature were 300 °C. Identification of each separated compound was achieved in comparison to the NIST08 mass spectrum library.

2.6. Thermo-gravimetric experiments

Thermo-gravimetric experiments of YLC were carried out on a Mettler-Toledo TGA/SDTA 851e thermobalance (Bruker, Germany). The catalysts were physically mixed with coal at a weight ratio of 1:20. 10 mg sample was placed in a 70 μL alumina crucible, and pyrolyzed at a constant heating rate of 10 °C min^{-1} from 40 to 800 °C under 100 mL min^{-1} H_2/N_2 (5%) atmosphere.

2.7. Calculation method of products yields

Throughout of this work, the yields of char, tar and gas in dry basis were defined as:

$$Y_{tar} = \frac{W_{tar}}{W_d} \times 100\%$$

$$Y_{char} = \frac{W_{char}}{W_d} \times 100\%$$

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

Sample	Proximate Analysis (ad)				Ultimate Analysis (ad)				
	M	A	V	FC	C	H	N	S	O[a]
YLC	3.70	6.74	34.31	55.25	70.28	3.87	1.13	0.54	13.74

ad: air dried base; M: moisture; A: ash; V: volatile matter; FC: fixed carbon.
[a] Calculated by difference.