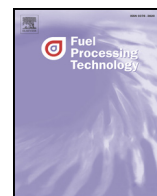




Contents lists available at ScienceDirect

## Fuel Processing Technology

journal homepage: [www.elsevier.com/locate/fuproc](http://www.elsevier.com/locate/fuproc)

# Catalytic upgrading of gaseous tars over zeolite catalysts during coal pyrolysis

Lun-Jing Yan, Xiao-Jun Kong, Rui-Fang Zhao, Fan Li\*, Ke-Chang Xie

State Key Laboratory Breeding Base of Coal Science and Technology Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China

### ARTICLE INFO

#### Article history:

Received 15 December 2014

Received in revised form 26 May 2015

Accepted 28 May 2015

Available online xxx

#### Keywords:

Coal pyrolysis

Tar upgrading

Heavy compounds

Light arenes

Zeolite catalysts

### ABSTRACT

Although light arenes such as benzene, toluene, and xylene in coal tar are widely used in industries, their amounts are relatively small. The catalytic cracking method for gaseous tar is one of the promising techniques for upgrading tar, and the amounts of light arenes are improved. Therefore, the catalytic upgrading of gaseous tar using two different catalysts is investigated in this study; the variations of light arenes before and after catalytic cracking are determined. More importantly, the variation of heavy compounds in gaseous tar is analyzed, and also the catalytic cracking mechanism is elucidated. The results show that the amount of benzene increases by 500% under the action of USY zeolite, and the amount of other compounds such as toluene, ethylbenzene, xylene, and naphthalene also increases by different degrees. However, Al/SBA-15 zeolite shows no obvious effect on gaseous tar upgrading. At the same time, the analysis results show that heavy compounds can be cracked over USY zeolite. Side chains are cleaved from aromatic rings, and aromatic rings are also cracked during the catalytic cracking reactions. Furthermore, light arenes are formed after the hydroxyl groups in phenols cleaved from the aromatic rings.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Pyrolysis is considered to be a promising method for coal conversion because tar, char, and gas are obtained. The light arenes in tar are widely used as industrial raw materials; for example, the benzene series are used for making plastics, rubbers, fibers, dyes, and pesticides. However, the amount of light arenes is relatively small, and that of heavy compounds (particularly pitch) is large [1]. The pitch is usually composed of tars with boiling points above 360 °C. These tars are condensed aromatics; therefore, they cannot be processed easily. The utilization efficiency of tar can be improved by converting heavy tars into the corresponding light arenes. The catalytic cracking method is one of the promising techniques for upgrading tar [2].

To improve the yields of light arenes in coal or biomass products, pyrolysis experiments have been performed by mixing coal with catalysts [3–7], thus affecting the pyrolysis behavior and product distribution and finally improving tar. For example, Ma et al. performed catalytic coal pyrolysis by mixing the coal with a catalyst in a fixed-bed reactor [3]; the yield of benzene, toluene, and xylenes in the products increased by catalytic cracking for coal pyrolysis over MoS<sub>2</sub> catalyst. However, the catalyst and coal char could not be separated from each other. This problem can be solved by the catalytic upgrading of gaseous tar during coal pyrolysis, resulting in high yields of light arenes.

The catalytic upgrading of gaseous tar has been investigated [2, 8–14]. For example, Wang et al. [8] performed catalytic in-situ tar reforming reactions during the pyrolysis and gasification of brown coal using a char-based catalyst in a two-stage reactor. The results show that activated char has good activity. The amount of tar decreased, while that of light arenes in the products increased. Li et al. [9] studied the catalytic cracking nascent coal volatiles using Indonesian natural limonite ore as the catalyst in a two-stage fixed-bed reactor, and finally the yields of light gases such as CH<sub>4</sub> and CO increased. The catalytic cracking of gaseous heavy tars during coal pyrolysis is of great significance. However, to the best of our knowledge, the distributions of heavy compounds in coal pyrolysis products before and after catalytic cracking have been rarely reported.

Therefore, in this study, the catalytic upgrading of gaseous tars using two different catalysts was investigated, and the variations in light arenes were compared. Moreover, the distributions of heavy compounds in gaseous tar were analyzed, and the catalytic cracking mechanism was elucidated.

## 2. Experimental

### 2.1. Coal samples

Fenxi bituminous coal (FBC, collected from Fenxi Coal Mine in Shanxi Province, China) was used in this study. It was ground and sieved to 0.15–0.30 mm. Table 1 shows the proximate and ultimate analyses of FBC.

\* Corresponding author.

E-mail address: [lifan66@hotmail.com](mailto:lifan66@hotmail.com) (F. Li).

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

Proximate analysis			Ultimate analysis (daf)				
$M_{ad}$	$A_d$	$VM_{daf}$	C	H	N	S	O <sup>a</sup>
0.5	7.6	26.4	86.5	4.0	1.2	1.7	6.6

Note: ad: air dry; daf: dry-and-ash-free basis.

<sup>a</sup> By difference.

## 2.2. Py-GC/MS experiment

Py-GC/MS experiments were carried out using a CDS Pyro-probe 5250. Approximately 1 mg of the coal sample was placed in a quartz tube. Catalyst (0.6 mg) was placed under the coal sample, and quartz wool was used to separate the layers of coal and catalyst, based on a sample loading diagram reported in the literature [11]. Helium (99.999%) was used as the carrier gas to purge the pyrolysis products to the GC. The pyrolysis temperature was set at 700 °C; the heating rate was 10,000 °C/s.

The pyrolysis products were analyzed using a Focus gas chromatograph and DSQ-II mass spectrometer (Thermo Fisher Scientific, USA). A DB-5MS capillary column (Thermo Fisher Scientific, USA) was used as the GC column. Helium was used as the GC carrier gas at an injection rate of 1 ml/min, and the split ratio was 1:70. The oven temperature program was set as follows: 40 °C for 4 min, heated to 70 °C at a rate of 4 °C/min (held for 2 min), heated to 200 °C at a rate of 10 °C/min (held for 3 min), and finally heated to 300 °C at a rate of 4 °C/min (held for 5 min). The injection and ion-source temperatures were set at 250 °C. The pyrolysis products were analyzed using a mass spectrometer in the electron ionization (EI) mode at 70 eV from  $m/z$  50 to 600 with a speed of 3000 amu/s. The chromatographic peaks were identified using the NIST MS library and chemical standards. To ensure that the results are reproducible, all the experiments were performed more than four times.

2-Ethyltoluene, 3-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 4-ethyl-*o*-xylene, 2-ethylnaphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,7-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1,6,7-trimethylnaphthalene, anthracene, phenanthrene, 1-methylantracene, 2-methylphenanthrene, 4-methyl-1,1'-biphenyl, 2,3'-dimethyl-1,1'-biphenyl, and 2-phenylnaphthalene were selected as the heavy compounds for this study. Phenol, *m/p*-cresol, *o*-cresol, 2,6-xyleneol, 3,4-xyleneol, 2,4-xyleneol, 2,4,6-trimethylphenol, and 2-methylnaphthalen-1-ol were also analyzed. Benzene, toluene, ethylbenzene, xylene and naphthalene (BTEXN) were selected as the light arenes.

## 2.3. Characterization of zeolite catalysts

Ultrastable Y-type (USY) zeolite was purchased from the Catalyst Plant of Nankai University (Tianjin, China), and SBA-15 zeolite was purchased from Jcnano Company (Nanjing, China). Al/SBA-15 zeolite was prepared by the incipient wetness impregnation method. SBA-15 zeolite was impregnated with an aqueous solution of  $Al(NO_3)_3 \cdot 9H_2O$  at room temperature for 24 h, dried at 100 °C for 7 h, and then calcined at 550 °C for 6 h in air.

The Si/Al ratio of the zeolites was measured by inductively coupled plasma atomic emission spectroscopy using a Thermo Icap 6300 spectrometer. The textural properties of the catalysts were determined using a Jwbk122w micropore analyzer (Beijing Jwgb Sci. & Tech. Co., Ltd., China), and the surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The pore volume, mean pore diameter, and most probable diameter were calculated using the Barrett–Joyner–Halenda (BJH) method.

The acidity of the zeolites were measured by temperature programmed desorption of ammonia ( $NH_3$ -TPD) in an apparatus. A sample

of 0.100 g  $\pm$  0.0002 g was placed in the quartz tube. The sample was heated to 200 °C for 120 min under helium flow before exposure to 10%  $NH_3$  at room temperature for 120–180 min. The  $NH_3$ -TPD curves for the zeolites were recorded from 50 to 800 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were measured using a Shimadzu XRD-6000 diffractometer equipped with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 KV and 30 mA. The scanning range of small-angle pattern was  $2\theta = 0.7$ – $7^\circ$  with a step size of  $2^\circ$ /min. The coking deposition on the catalyst was analyzed using Netzsch 449 F3 thermo-gravimetric analyzer. The used catalyst (20 mg) was placed on the sample plate, and then it would be heated to 700 °C at heating rate of 10 °C/min. The flow rate of  $O_2$  and  $N_2$  was 20 and 80 ml/min, respectively.

## 3. Results and discussion

### 3.1. Structure of zeolite catalysts

As Fig. 1 shows, a very strong diffraction peak at  $2\theta = 1.02^\circ$  (100) and two weak diffraction peaks at  $2\theta = 1.7^\circ$  (110) and  $1.92^\circ$  (200) are observed, indicating that SBA-15 and Al/SBA-15 zeolites have a typical hexagonal structure [15]. Al/SBA-15 zeolite retains the ordered structure after  $Al_2O_3$  supported. Furthermore, the loading amount of Al on Al/SBA-15 zeolite determined by the ICP test is 12.6%, and the Si/Al ratio of USY zeolite is about 4.3.

Compared to SBA-15 zeolite, the surface area and pore volume of Al/SBA-15 zeolite decrease, as shown in Table 2. This is mainly because Al entered into the channels of SBA-15 zeolite [16]. On the one hand, Al/SBA-15 zeolite has a high pore volume (0.5 cm<sup>3</sup>/g), while USY zeolite has a pore volume of only 0.1 cm<sup>3</sup>/g. On the other hand, the average pore and most probable diameters of USY zeolite are 2.5 and 1.9 nm, respectively, whereas those of Al/SBA-15 zeolite are obviously higher. Therefore, heavy compounds easily enter into the zeolite channels and undergo catalytic cracking at the active sites when Al/SBA-15 zeolite is used as the catalyst.

### 3.2. Formation of BTEXN over USY and Al/SBA-15 zeolites

The amount of light arenes in the products increases by 130% after catalytic cracking of gaseous tar over USY zeolite, whereas only 30% increase is observed for Al/SBA-15 zeolite, as shown in Fig. 2. The amounts of benzene, toluene, xylene, ethylbenzene, and naphthalene increase by different degrees over USY zeolite, as demonstrated in Fig. 3. The amounts of benzene and toluene increase by almost 500% and 150%, respectively, while the amounts of arenes with a relatively long side chain such as xylene or ethylbenzene increase slightly. The reason is that xylene and ethylbenzene can crack to form simpler arenes

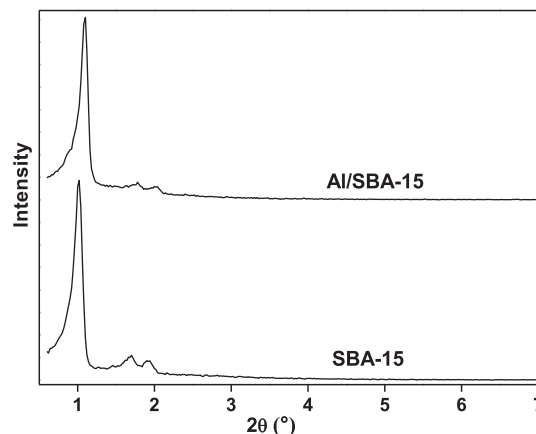


Fig. 1. Small-angle XRD patterns of SBA-15 and Al/SBA-15 zeolites.

Download English Version:

<https://daneshyari.com/en/article/6656869>

Download Persian Version:

<https://daneshyari.com/article/6656869>

[Daneshyari.com](https://daneshyari.com)