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Research article

In-situ catalytic upgrading of coal pyrolysis tar coupled with CO_2 reforming of methane over Ni-based catalysts

Mingyi Wang, Lijun Jin, Yang Li, Jiannan Lv, Baoyong Wei, Haoquan Hu*

State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Tar was upgraded by integrating in-situ catalytic cracking of coal pyrolysis tar with CO_2 reforming of methane (CRM) over Ni-based catalysts to improve light tar yield. The results showed that Ni-based catalysts can catalyze coal tar cracking and CRM simultaneously, and some radicals, like $\cdot$H and $\cdot CH_x$, produced in CRM over Ni-based catalysts could combine with the radicals from catalytic cracking of tar to avoid excessive cracking of tar. The catalyst $5Ni/Al_2O_3$ (Ni/Al_2O_3 with 5 wt% Ni) showed the best performance for tar upgrading owing to its appropriate activity of both tar cracking and CRM. Compared with non-upgrading tar, the average molecular weight of upgrading tar over $5Ni/Al_2O_3$ decreases from 279 to 193 amu, and the content and yield of light tar (boiling point $<$ 360 °C) over $5Ni/Al_2O_3$ increase by 53% and 32% at 650 °C. The contents of light fractions increase and that of pitch decreases apparently. The light components, such as benzenes, phenols and naphthalenes, are all improved, and long aliphatic chains and aromatics with 3 or 4 rings have an obvious decrease. Active components in upgrading catalysts obviously affect the upgrading effect of coal tar. $5Ni/Al_2O_3$ exhibits higher content and yield of light tar compared with $5Co/Al_2O_3$ and $5Fe/Al_2O_3$.

1. Introduction

Pyrolysis, as one of clean and efficient technologies for coal conversion, can produce gases, char and tar. But low molar ratio of hydrogen to carbon in coal leads to a large amount of heavy components in the pyrolysis tar, along with high viscosity and corrosion [1]. Therefore, it is top priority to convert the heavy components into light tar and pyrolysis gases.

Catalytic cracking has been proved an effective method to reduce heavy tar from coal and biomass. Han et al. [2] investigated catalytic cracking effect of Fugu coal pyrolysis tar over different metal-loaded char catalysts and found that all the catalysts could lead to lower tar yield but higher light tar content. Compared with Co-, Cu- and Zn-loaded char, Ni/char could maximize light tar yield. Veses et al. [3] conducted catalytic cracking of biomass pyrolysis vapors over different metal-loaded ZSM-5 zeolites. When Ni/ZSM-5 and Sn/ZSM-5 were used, the decrease of viscosity and acidic compounds in bio-oil was found, and the aromatic fractions were improved. They also tested catalytic effect of bio-oil over sepiolite, bentonite and attapulgite, and found these low cost materials could reduce the viscosity of the obtained bio-oil and improve the stability of organic fractions [4]. Jin et al. [5] focused on catalytic cracking of Shenmu coal pyrolysis tar over two different carbon-based catalysts. The results showed that commercial AC exhibits better catalytic effect than char, mainly because of its higher specific surface area. Le et al. [6] also investigated the catalytic cracking process of Shenmu coal pyrolysis tar. USY zeolite, CaO and K_2CO_3 were mixed with coal sample, respectively, and the light tar yield increased from 9.5 to 11.1 wt% when USY was used as the catalyst. Lai et al. [7] focused on catalytic cracking of shale oil over shale ash, and concluded that the ash could increase the gasoline and diesel content by about 45%. Liu et al. [8] used a drop tube reactor to investigate catalytic cracking effect of different metal-loaded HZSM-5 zeolites. During catalytic cracking of Ni/HZSM-5, the aromatics content in Shengli pyrolysis tar exceeds 90 wt%, higher than that over Co- and Mo/HZSM-5, but the total tar yield decreases apparently.

However, the above-mentioned catalytic cracking process always happened in N_2 atmosphere, and it could not avoid excessive cracking of pyrolysis tar because upgrading tar is a progress of the increasing H/C molar ratio in tar. Therefore, it is profitable to retard the decrease of tar yield when some H-rich radicals are added to stabilize the cracking radicals from coal tar. Hydrogen was used to hinder the excessive cracking and improve tar yield [9,10], but its cost was too expensive. Methane with a high H/C molar ratio could be the hydrogen substitute, and generate free radicals through catalytic reforming reactions [11]. Therefore, it seems a promising route to increase the content and yield of light tar when the free radicals from CH_4 activation participate the

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* Corresponding author.
E-mail address: hhu@dlut.edu.cn (H. Hu).

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decomposition of coal tar. CO_2 reforming of methane (CRM) is an appropriate way to activate and utilize methane, and has been widely studied [12–18]. Xu et al. [14] compared reforming effect of several activated carbon (AC) based catalysts. At 700 °C, the average conversions of CH_4 and CO_2 over AC/$NaNO_3$ are 17.7% and 29.7%, respectively, much higher than those over AC. Compared with carbon-based catalysts, metal catalysts always have higher activity [15,19]. Among numerous metal catalysts, transition metals attracted much more attention than noble metals (Ru, Rh and Pt) based on the relative cheap cost at industrial application [18]. Akbari et al. [16] conducted the reforming effect of Ni-MgO-Al_2O_3 catalyst with various Ni loadings. The results showed that within a certain range, more accessible Ni active sites could increase the catalytic activity, and the Ni loading of 15 wt% was suitable. Lin et al. [17] obtained a similar result, and considering coke resistant and catalyst stability at high temperature, the optimal Ni content was 12 wt%. Jin et al. [19] used sucrose as carbon source to prepare carbon-Ni/MgO-Al_2O_3 composite catalyst, and the resistance carbon deposition ability of this catalyst were much better than Ni/MgO-Al_2O_3.

Our previous researches have proved that integrated coal pyrolysis with CRM is an effective way to increase tar yield, and quite a bit CH_4 and CO_2 were not converted during this process [20,21], so we can just use this part of CH_4 and CO_2 in tar upgrading process. In this paper, a novel tar catalytic upgrading process was put forward, which combined catalytic cracking of coal pyrolysis tar with CO_2 reforming of methane, expecting that excessive cracking of tar can be restricted and more light tar was obtained.

2. Experimental

2.1. Coal and catalyst preparation

The Buliangou (BLG) subbituminous coal from Inner Mongolia was selected in this work. Before the pyrolysis experiment, BLG coal was crushed, sieved to the particle size of below 0.178 mm and dried under vacuum at 65 °C for 24 h. The proximate and ultimate analyses of BLG coal are listed in Table 1.

The upgrading catalyst was prepared by dispersing Al_2O_3 into a deionized aqueous solution containing a certain concentration of transition metal (Fe, Co, Ni) nitrate. Ni loading is x wt% (x = 3–10). After being stirred at 60 °C for 4 h to enhance the dispersion of the transition metal, water in the mixture was removed by a rotary evaporator under vacuum at 65 °C for 4 h and the catalyst was calcined at 800 °C in air for 4 h. Finally, the catalyst was crushed and sieved to below 0.178 mm, and reduced at 650 °C in H_2 for 4 h. The resultant catalyst is labelled as xNi/Al_2O_3. For comparison, the Fe and Co loading in catalysts were fixed at 5 wt%, the prepared catalysts are expressed as 5Fe/Al_2O_3 and 5Co/Al_2O_3. The textural properties of metal catalysts were carried out by N_2 adsorption at −196 °C with a physical adsorption apparatus (JW-BK200A), and the surface area and pore information were obtained by using BET and BJH methods.

2.2. Experimental apparatus and procedure

In-situ catalytic upgrading of coal pyrolysis tar was performed in a vertical fixed-bed reactor (length of 290 mm and inner diameter of 14 mm), as shown in Fig. 1. In each run, 1 g of reforming catalyst (a commercial Ni/Al_2O_3 catalyst with 20 wt% of Ni content), 5 g of BLG coal and 1 g of upgrading catalyst were filled into the reactor and separated to three layers by some quartz wool [22]. Before the pyrolysis experiment, a mixture of CH_4/CO_2/N_2 was introduced into the reactor and the flow rates of CH_4/CO_2/N_2 were 120, 120 and 60 ml/min, respectively. The reactor was heated to the setting temperature within 10 min and kept for 30 min. Liquid products was collected by a cold trap (−15 °C), and the non-condensable gases was analyzed by GC.

Table 1
Proximate and ultimate analyses of BLG coal.

Proximate analysis (wt%)			Ultimate analysis (wt% daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O[a]
2.11	15.37	37.68	77.50	4.62	1.27	0.84	15.77

[a] By difference.

2.3. Analyses of tar and gases

The quality of the tar in each experiment was evaluated by simulated distillation gas chromatograph, gel permeation chromatography (GPC), gas chromatography/mass spectrometry (GC/MS) and nuclear magnetic resonance (NMR).

The boiling point analysis of tar was identified by simulated distillation GC (SCION 456-GC with CP-SimDist column) according to ASTM 2887. The light tar content refers to the total fractions with boiling point below 360 °C, including light oil, phenol oil, naphthalene oil, wash oil and anthracene oil, which the boiling point range is below 170 °C, 170–210 °C, 210–230 °C, 230–300 °C and 300–360 °C, respectively. The heavy fractions of tar with boiling point above 360 °C are called pitch. Before analysis, the tar was first dissolved in carbon disulfide, and then Na_2SO_4 was added to adsorb the water in tar. After filtration to remove Na_2SO_4, the tar was concentrated by a rotary evaporator to remove most of carbon disulfide.

The molecular weight of tar was measured by GPC according to the principle that larger molecular size (three-dimensional volumes) sample elutes faster from the column. The solvent delivery pump was Waters 1525 and the mobile phase was tetrahydrofuran. Tar components and their contents were determined by GC/MS (Agilent 6890 N GC coupled with an Agilent 5975 mass detector) and GC, respectively. Each compound was identified by the match of the standard spectrum in NIST 2000 spectral library, and its content was achieved by GC through an area normalization method [23].

Hydrogen and carbon distribution information of tars was performed by ^{1}H NMR and ^{13}C NMR spectra (Bruker AvanceII400M) using $CDCl_3$ as solvent and TMS as the chemical shift reference. The concentration of tar sample was about 0.1 g/ml.

Tar and water were separated according to ASTM D95-05^{e1} (2005) by toluene as solvent. Tar yield (Y_{tar}) and light tar yield ($Y_{light\ tar}$) in dry ash-free basis were calculated as follows:

$$Y_{tar} = \frac{W_{tar}}{W_o \times (1 - A_{ad} - M_{ad})} \times 100\%$$

$$Y_{light\ tar} = Y_{tar} \times w_1\%$$

where, W_{tar} and W_O are the weight of tar and coal sample; A_{ad} and M_{ad} are the ash and moisture contents of coal; w_1% is light tar content. Tar yield and light tar content are the average values of at least three equivalent experiments, and the experimental relative error was within ± 2%.

Pyrolysis gases were analyzed by gas chromatography (GC7890 II), and the detailed operations were described in our previous study [5].

3. Results and discussion

3.1. Upgrading effect of Ni-based catalysts

3.1.1. Effect of commercial Ni/Al_2O_3 catalyst on tar upgrading

The commercial Ni/Al_2O_3 catalyst was used to catalyze CRM process before coal pyrolysis. Because Ni-based catalysts also have activity to tar cracking, catalytic upgrading of coal pyrolysis tar over the commercial Ni/Al_2O_3 catalyst was investigated first.

Tar yield, light tar content and yield from coal pyrolysis with or