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Light fraction from catalytic hydroconversion of two Chinese coals in cyclohexane over a solid acid

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ABSTRACT

Two Chinese coals, Shengli lignite and Shenmu–Fugu subbituminous coal, were subjected to non-catalytic hydroconversion (NCHC) and catalytic hydroconversion (CHC) in cyclohexane at 300 °C for 3 h under pressurized hydrogen using a solid acid as the catalyst, which was prepared by impregnating isometric pentachloroantimony and trimethylsilyl trifluoromethanesulfonate into an activated carbon. The reaction mixtures from both NCHC and CHC were sequentially extracted with petroleum ether, carbon disulfide, methanol, acetone, and isometric acetone/carbon disulfide mixed solvent to afford extracts 1–5 (E_1–E_5). The results show that both E_1 and total extract yields from CHC are appreciably higher than those from NCHC of each coal. E_1 from either NCHC or CHC of each coal was analyzed with a gas chromatograph/mass spectrometer (GC/MS) and an atmospheric solids analysis probe/time of flight mass spectrometer (ASAP/TOF-MS). GC/MS analysis shows that each E_1 consists of alkanes, arenes, and oxygen-containing organic compounds (OCOCs), and most of the arenes are methyl-substituted ones, whereas alkenyl groups only appear on benzene ring; most of the OCOCs are arenols, especially alkylarenols. According to ASAP/TOF-MS analysis, organic compounds with molecular masses ranging from 500 to 950 *u* appear in E_1 from CHC of both coals.

1. Introduction

Coals were primary sources of feedstocks for manufacturing a wide range of organic chemicals until the early 20th century when cheap and easy-to-process petroleum became available [1]. With the depletion of the conventional petroleum resources, coals are likely to play an important role in the chemical industry again [2]. Direct coal liquefaction (DCL), in which coals are liquefied directly into liquid fuels or chemicals by catalytic hydrocracking or hydrogenation [3,4], is a promising process for a clean and effective utilization of coals [5].

The most common catalysts for DCL are iron sulfides. The process converting iron sulfides into pyrrhotites was considered to be a significant step in the catalytic hydrocracking or hydrogenation of coals and the reactions are often limited by the dispersion of the catalytically active pyrrhotite particles [4,5], while the reactions of diarylmethanes used as coal-related model compounds (CRMCs) proved that iron sulfides catalyzed the formation of hydrogen radicals, which played a crucial role in cleaving bridged bonds (BBs) in the CRMCs [3,6]. Many investigations focused on the improvement of catalyst dispersibility to improve the effectiveness of the iron catalysts [7–12]. In addition, many other metals, such as well dispersed Mo and Ni, which can be more easily dispersed, were also used as active species of catalysts for DCL [13].

MoS_2 and $ZnCl_2$ were used to catalyze hydropyrolysis of five Chinese coals to improve the yields of benzene, toluene, and xylene [14]. SO_4^{2-}/ZrO_2 was also applied to catalyze CRMC hydrocracking at temperatures up to 435 °C and the hydrocracking was thought to occur via the carbenium ion mechanism [15]. The catalytic activity of SO_4^{2-}/ZrO_2 was compared with those of FeS and FeS + S and it was concluded that the catalyst acidity played an important role in the C–C bond cleavage and the hydrogenation ability of the catalyst was important for the C–O bond cleavage [16–18].

Trifluoromethylated compounds were of particular interest for the strong electron-withdrawing effect of the CF_3 group [19], and trifluoromethanesulfonic acid was found to solubilize lignite and subbituminous coal in the presence of isopentane at temperatures as low as 150 °C for 3 h under autogenous pressure of 6.1–6.9 MPa without hydrogen [20–22]. Pentachloroantimony (PCA) and trimethylsilyl trifluoromethanesulfonate (TMSTFMS) were also used as precursors of active species to prepare solid acids (SAs) by impregnating into an activated carbon (AC), and PCA and TMSTFMS exhibited significantly synergic effect on di(1-naphthyl)methane (DNM) hydrocracking under relatively mild conditions [23,24].

Selective coal conversion is possible under desired reaction conditions in the presence of an appropriate catalyst [25]. Metal sulfides selectively catalyzed DNM hydrocracking via monatomic hydrogen

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transfer, i.e., radical hydrogen transfer, to the *ipso*-position of DNM [3,25,26], whereas SAs catalyzed hydrocracking via a cationic mechanism [27]. The different forms of active hydrogen involved in the reactions may lead to different products.

The derivates from DCL are very complex and thereby difficult to be isolated and separated [28]. Identification of the products not only is important for effective utilization of the derivates but also provides important information about the reaction mechanisms and facilitates improving DCL process.

Gas chromatograph/mass spectrometer (GC/MS) has been widely applied in identifying coal derivates [29–31], but faces difficulty in detecting less volatile, thermally labile, and/or strongly polar species. Atmospheric solids analysis probe/time of flight-mass spectrometer (ASAP/TOF-MS) was successfully used to analyze CRMCs [32,33] and coal derivates [33–35]. Some of the detected compounds are less volatile, thermally labile, and/or strongly polar species. Therefore, more useful information on molecular composition (MC) of coal derivates could be acquired by flexible use of GC/MS and ASAP/TOF-MS.

In the present investigation, we used a SA as the catalyst and examined the compositional features of light fractions (LFs) from non-catalytic hydroconversion (NCHC) and catalytic hydroconversion (CHC) of two Chinese coals under relatively mild conditions.

2. Experimental

The two Chinese coals are Shengli lignite (SL) and Shenmu–Fugu subbituminous coal (SFSBC) collected from Xilinhaote, Inner Mongolia and Northern Shanxi, respectively. They were pulverized to pass through a 200-mesh sieve followed by desiccation in a vacuum at 80 °C for 24 h before use. Table 1 shows their ultimate and proximate analyses. All the reagents used in the experiments are commercially purchased analytical reagents, among which cyclohexane, petroleum ether (PE, bp. 30–60 °C), carbon disulfide (CDS), methanol, and acetone were purified by distillation with a Büchi R-210 rotary evaporator prior to use. The SA was prepared by impregnating isometric PCA and TMSTFMS into AC under microwave irradiation and subsequent treatments, as previously reported [23].

About 1 g coal samples, 0 or 0.4 g SA, and 30 mL cyclohexane were placed into a 60 mL stainless steel, magnetically stirred autoclave. After replacing air in the autoclave with hydrogen, the autoclave was pressurized with hydrogen to 5 MPa at room temperature and heated to 300 °C within 15 min. After reaction at 300 °C for 3 h, the autoclave was rapidly cooled in an ice-water bath to room temperature. The reaction mixture was taken out from the autoclave and transferred into a cylindrical paper filter placed in a Soxhlet extractor and sequentially extracted with PE, CDS, methanol, acetone, and isometric acetone/carbon disulfide mixed solvent to afford extracts 1–5 (E_1–E_5), respectively. The coals, extracts, and residues were analyzed with a Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer by collecting 50 scans at a resolution of 8 cm^{-1} in reflectance mode with measuring regions of 4000–400 cm^{-1}. The extracts were also analyzed with a Hewlett-Packard 6890/5973 GC/MS and an IonSense/Agilent 6210 ASAP/TOF-MS. The GC/MS is equipped with a capillary column coated with HP-5MS (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, 0.25 m film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. Compounds were identified by comparing mass spectra with NIST05a library data. The ASAP/TOF-MS is equipped with an atmosphere pressure chemical ionization ion source. The corona discharge (CDC) current and capillary voltage were set to 4.0 uA and 4 kV, respectively. The hot nitrogen stream and drying gas temperatures were set to 250 °C and 350 °C, respectively. The capillary tube with E_1 was inserted into the ion source. The hot nitrogen gas from the electrospray probe directs molecules in the gas phase toward the CDC to create either protonated molecular ions or radical molecular cations that are subsequently analyzed. The operation was run in positive mode and the m/z range was set from 100 to 1000.

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

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C
	M_{ad}	A_d	V_{daf}	C	H	N	$O_{diff.}$		
SL	12.52	16.69	43.44	74.29	4.27	1.08	>19.42	0.94	0.6850
SFSBC	5.33	6.32	30.47	79.82	4.73	1.05	>13.90	0.50	0.7062

3. Results and discussion

3.1. Extract yields

As shown in Fig. 1, the total extract yield from CHC of each coal exceeded 60% of organic matter (OM) in the coal and is obviously higher than that from NCHC of the coal, suggesting that CHC obviously increased the solubility of OM in both coals. The yields of E_1 as the LF increased from 3.9% and 5.8% obtained by NCHC of SFSBC and SL to 7.0% and 9.6% obtained by CHC of SFSBC and SL, respectively.

3.2. Differences in structural feature among SL, SFSBC, and extracts and residues from NCHC and CHC of the two coals

The absorbances around 2913, 2845, and 1420 cm^{-1} in Fig. 2 are ascribed to the vibrations of aliphatic moieties (AMs). These absorbances from E_1 and E_2 are significantly stronger than those from other samples, suggesting that both NHCH and CHC resulted in the increase of AM-containing species (AMCSs) and the AMCSs were selectively extracted by PE and CDS. Compared to NCHC, an appreciable increase in these absorbances in FTIR spectra of E_1 and E_2 from CHC of both coals can also be observed. In contrast, other extracts seem to be rich in polar groups (PGs), such as hydroxy group with absorbance around 3412 cm^{-1} and ester group with absorbances around 1220 and 1142 cm^{-1}, since the PG-containing species tend to be extracted by polar solvents, such as methanol and acetone.

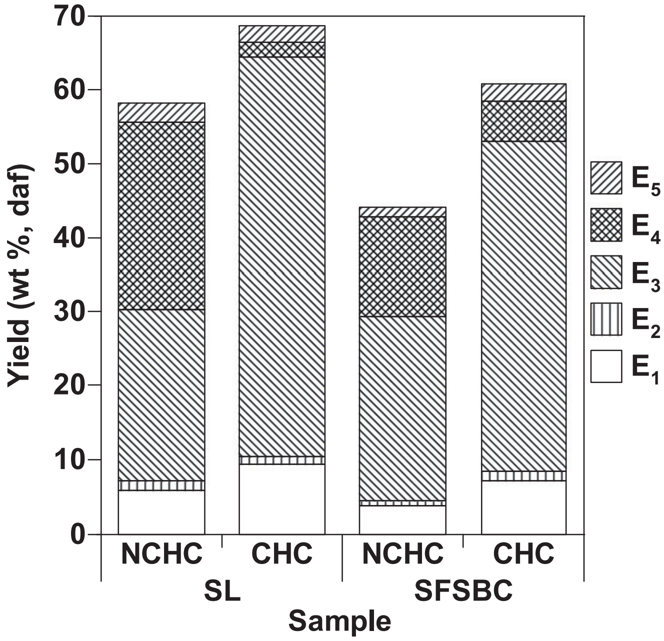

Fig. 1. Yields of the extracts from NCHC and CHC of the two coals.