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Advances in Lignite Extraction and Conversion under Mild Conditions

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ABSTRACT: Lignites are abundant coal resources, but they are low-quality fuel for direct combustion because of their high moisture content, high ash yield, and low calorific value. Upgrading technologies for lignites such as drying and pyrolysis have been widely investigated. Lignite conversion under mild conditions for producing ash-free coals, value-added chemicals, and/or liquid fuels also deserves attention. This paper reviews recent developments in extraction and mild conversion of lignites. The related techniques, including sequential extraction, thermal dissolution, mild oxidation, and catalytic hydroconversion of lignites, are described in detail. In addition, the application of high-resolution mass spectrometry in determining lignite-derived products is presented. Future investigations on efficient utilization of lignites are also suggested.

1. INTRODUCTION

With the dramatically shrinking amount and unbalanced distribution of petroleum, coal conversion into liquid fuels, materials, and chemicals has attracted increasing attention.[1−5] Coal reserve is abundant, and ca. 40% of the total coal deposits are lignites, the reserve of which is estimated to be more than 4 trillion tons over the world.[6] Therefore, it is imperative that lignites should be used efficiently. However, their high ash yield, high moisture content, and low calorific value limit the industrial application of lignites, especially for electric power generation.[7] On the other hand, due to their higher H/C ratio and oxygen content than high-rank coals, lignites have intrinsic advantages as feedstocks for liquid fuels and chemicals. The efficient utilization of lignite resources should be clean, limited, and value-added.

Extensive research on drying,[8] pyrolysis,[9] combustion,[10] and liquefaction[11−13] of lignites has been conducted in the past decades. Lignite extraction and conversion under mild conditions (<400 °C and <15 MPa), including sequential extraction, thermal dissolution, oxidation, and catalytic hydroconversion, also deserve attention. Using extraction/thermal dissolution and subsequent column chromatography, many valuable chemicals can be enriched and isolated from lignites.[14,15] Although the yield from lignite extraction is usually low, obtaining lignite extracts is much easier than obtaining other lignite-derived liquids. In addition, thermal dissolution of lignites can also be used to produce HyperCoals (ash-free coals), and the ash content of the HyperCoals is generally less than 200 ppm (total content of Na and K is less than 0.5 ppm).[16] Mild oxidation of lignites is not only an important method to study the chemical structures but also a promising way to yield carboxylic acids, including fatty acids (e.g., oxalic acid, malonic acid, and succinic acid) and benzenecarboxylic acids (BCAs).[17,18] Effectively cleaving C−C and/or C−O bridged bonds in lignites via catalytic hydroconversion is also crucial for converting lignites into fuels or chemicals.

As listed in Table 1, the contents of carbon and oxygen vary in different lignites. In this Review, the developments of lignite extraction and conversion under mild conditions, including sequential extraction, thermal dissolution, oxidation, and catalytic hydroconversion, along with the resulting product identification and primary isolation are described. Prospects and future challenges involved in such processes are also presented.

2. EXTRACTION AND THERMAL DISSOLUTION OF LIGNITES

2.1. Extraction. As a nondestructive and separable method, extraction was widely used to isolate inherent components in coals.[33] Many organic solvents, such as n-hexane, carbon disulfide, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran, N-methyl-2-pyrrolidinone (NMP), pyridine, and quinoline have been used for coal extraction.[34] It is generally believed that pyridine, tetrahydrofuran, and NMP usually give higher extract yields, and mixed solvents are often more effective than a single solvent for coal extraction. The famous isometric carbon disulfide/NMP mixed solvent found by Iino et al.[35] proved to be very effective for extracting organic matter from bituminous coals. The extract yields of Zaozhuang and Upper Freeport bituminous coals using carbon disulfide/NMP as the solvent unexpectedly reach up to 65.6% and 54.0%, respectively.[35] However, lignites gave much lower extract yields than bituminous coals in the same mixed solvent, as shown in Table 2. The lower extract yields of lignites than those of bituminous coals are probably related to the larger portion of macromolecular moiety in lignites than in bituminous coals.[36] Takanohashi et al.[37] examined extraction behaviors of Loy Yang lignite in various solvents under ultrasonic irradiation. They found that polar solvents such as NMP, pyridine, and methanol gave higher extract yields than nonpolar solvents (Table 2). Lignite extracts usually contain numerous organic compounds, most of which are value-added ones. Nevertheless, it is

Table 1. Proximate and Ultimate Analyses (wt%) of Lignites Used in This Review[a]

lignite	country	proximate analysis			ultimate analysis (daf)					
		M_{ad}	A_d	VM_{daf}	C	H	N	O[b]	$S_{t,d}$	ref
Zhaotong	China	11.6	21.0	53.6	52.5	3.3	1.0	>41.8	1.4	19
BL	Canada		19.2		54.3	3.9	1.2	>39.4	1.2	20
Soma	Turkey		22.1	51.1	58.4	4.5	1.2	>34.1	1.8	21
BD	Canada		15.3		58.6	4.2	1.3	>35.1	0.8	20
Çayırhan	Turkey		27.2	34.7	58.6	4.7	1.9	>28.4	6.4	21
Mequinenza	Spain		39.9		59.8	5.8	1.0	>19.7	13.7	22
Kangal	Turkey				62.4	5.4	1.9	>22.2	8.1	23
Xianfeng	China	33.6	18.5	60.6	63.1	6.0	1.8	>28.7	0.4	24
Mulia	Indonesia		3.2		65.5	5.0	0.9	>28.6	0.1	25
Loy Yang	Australia		1.5		66.9	4.7	0.7	27.7		26
Yallourn	Australia		1.6		66.9	4.7	0.5			27
Morwell	Australia		1.5	50.3	67.1	4.9	0.6	27.4		28
Banko 97	Indonesia		2.4		70.0	5.3	1.3	>23.1	0.3	29
Shengli	China	13.7	7.5	46.4	70.8	5.1	0.9	>21.9	1.3	30
South Banko	Indonesia		2.3		71.3	5.4	1.2			27
Beulah Zap	America		9.7	44.9	72.9	4.8	1.2	>20.3	0.8	17
Huolinguole	China	16.5	21.3	48.1	73.1	5.0	0.2	>20.6	1.1	31
Xiaolongtan	China	16.4	14.5	50.7	73.7	3.9	1.3	>20.1	1.0	32

[a]Abbreviations: M_{ad}, moisture (air-dried base); A_d, ash (dry base, i.e., moisture-free base); VM_{daf}, volatile matter (dry and ash-free base); daf, dry and ash-free base; $S_{t,d}$: total sulfur (dry base); [b]By difference.

Table 2. Extract Yields of Lignites under Different Conditions

lignite	solvent	method	yield (%)	reference
Loy Yang	CS₂/NMP	ultrasonic	5.1	Iino et al.,[35] 1988
Yallourn	CS₂/NMP	ultrasonic	6.4	
Loy Yang	NMP	ultrasonic	14.3	Takanohashi et al.,[37] 1996
	pyridine	ultrasonic	12.9	
	acetone	ultrasonic	7.7	
	methanol	ultrasonic	8.7	
	tetrahydrofuran	ultrasonic	5.5	
	benzene	ultrasonic	2.2	
	n-hexane	ultrasonic	<1.0	
Kangal	benzene	Soxhlet	2.7	Önal et al.,[23] 1997
	toluene	Soxhlet	3.2	
	pyridine	Soxhlet	7.8	
	tetrahydrofuran	Soxhlet	8.4	
Shengli	CS₂/acetone	ultrasonic	2.1	Cong et al.,[38] 2014

Figure 1. Yields of extracts from sequential ultrasonic extraction of Xianfeng lignite. Adapted with permission from ref 40.

extremely difficult to separate and identify these compounds due to the compositional complexity of the extracts.

Fractional extraction using different solvents proved to be an effective approach for increasing the extract yields of lignites and simultaneously separating the extractable organic matter into several fractions.[39,40] Nishioka[39] carried out fractional extraction of Beulah Zap lignite and found that up to 25% of soluble portion was obtained. Xianfeng lignite was sequentially extracted with petroleum ether, carbon disulfide, methanol, acetone, and isometric carbon disulfide/acetone mixed solvent under ultrasonic irradiation to afford extracts 1−5 (E_1−E_5), respectively.[40,41] In total, 13.7% of organic matter in Xianfeng lignite was extracted (Figure 1).[40] According to analysis with a gas chromatograph/mass spectrometer (GC/MS), the extracts consist of alkanes, cycloalkanes, alkenes, cycloalkenes, alkyl-
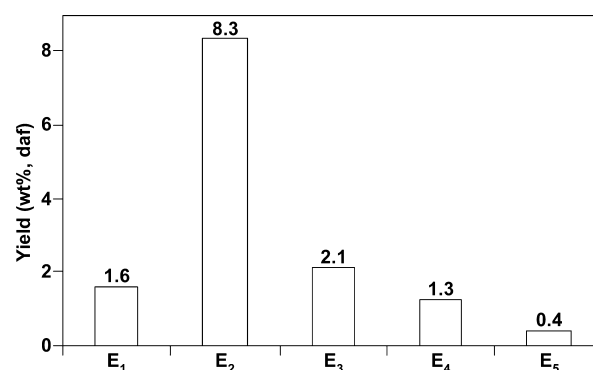
benzenes, condensed arenes, alcohols, aldehydes, ketones, carboxylic acids, esters, and nitrogen-containing species. Different from the extracts from higher-rank coals, such as Geting bituminous coal,[33] the extracts from Xianfeng lignite are mainly comprised of alkanes rather than condensed arenes. Taking E_1 as an example, alkanes show a bimodal distribution ranging from C_{13} to C_{33}, with maxima at C_{15} and C_{27}. The alkanes with C_{12}−C_{22} and those with C_{23}−C_{29} were reported to originate from lower (algae, bacteria/fungi, and lichen) and higher (bryophyte, pteridophyte, and spermatophyte) plants, respectively.[42]

A magnetically stirred extraction system with a polytetrafluoroethylene membrane filter (pore size of 0.45 μm) was developed and used for extracting relatively large amounts of coal samples.[14,33] About 1.5 kg of Shengli lignite was exhaustively extracted with isometric carbon disulfide/acetone mixed solvent to obtain the extract (ca. 31.8 g).[38] Using sequential extraction and subsequent column chromatography along with recrystallization, four arylhopanes (Figure 2),[38] including two novel phenylhopanes (22-phenyl-30-norhopane and 22-(o-tolyl)-30-norhopane) and two thienylhopanes (30-(5-methylthien-2-yl)hopane and 30-(thien-2-ylmethyl)hopane),
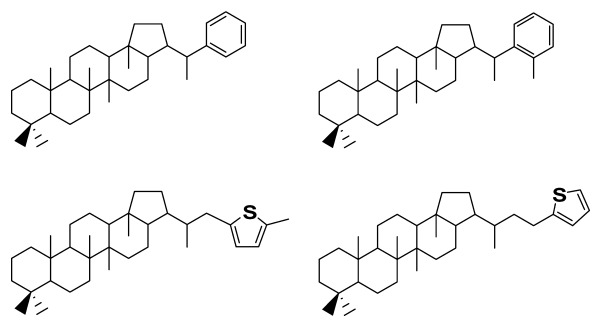
Figure 2. Four arylhopanes enriched from Shengli lignite.[38]

and 14 cyclized hopanoids,[43] including hydrobenzohopanes, benzohopanes, and rearranged benzohopanes, were enriched, and 3-ethyl-8-methyl-2,3-dihydro-1H-cyclopenta[a]chrysene (Figure 3)[14] was isolated from Shengli lignite. 3-Ethyl-8-
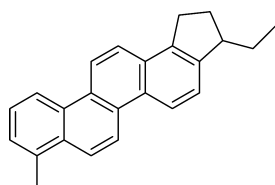

Figure 3. 3-Ethyl-8-methyl-2,3-dihydro-1H-cyclopenta[a]chrysene isolated from Shengli lignite.[14]

methyl-2,3-dihydro-1H-cyclopenta[a]chrysene is mainly produced from the demethylation of neohop-13(18)-ene and subsequent aromatization. Hopanoids play important roles in organisms, geochemistry, and petroleum exploration.[44,45] Understanding their cyclization process could provide some clues to the origin of arenes in coals. A novel type of cyclization reaction, i.e., cyclization at C30, for phenylhopane formation was proposed.[38]

2.2. Thermal Dissolution. In general, unlike bituminous coals, only small amount of organic matter can be extracted from lignites at room temperature, largely due to strong noncovalent interactions between small molecules and macromolecular network in lignites. Raising the extraction temperature could relax the interactions, resulting in higher extract yields. In the past decade, Japanese researchers have developed thermal dissolution processes for obtaining high extract yields and producing HyperCoals.[16,22,25,26,46−53] In 2002, Takanohashi et al.[46] first raised the concept of HyperCoal. They investigated the thermal dissolution behavior of different coals in tetralin, 1-methylnaphthalene, dimethylnaphthalene, and coal-derived oils at 200−380 °C. Their results exhibited that up to 80% of organic matter in the coals can be separated as HyperCoals with hot filtration after thermal dissolution in crude methylnaphthalene oil (CMNO) at 360 °C.[16] The high extract yield was ascribed to the solvent- and thermal-induced relaxation of coal aggregates by the nitrogen-containing species (mainly quinolines).[16] HyperCoals produced from different coals in 1-methylnaphthalene at 300−420 °C for 1 h were characterized using structural and thermal analyses.[25] The carbon type distributions in the HyperCoals obtained below 360 °C are similar to those in the corresponding raw coals. HyperCoal was reported to have potential uses as a clean fuel for gas turbines[47] and a raw material for carbon fuel cells,[54,55] gasification,[56,57] and high-performance carbon materials.[58] Compared with conventional direct coal liquefaction, thermal

dissolution of coals has some merits, such as a simpler process, milder conditions, and no consumption of catalyst and gaseous hydrogen.

As Table 3 exhibits, many efforts were made to examine thermal dissolution behaviors of various lignites in different solvents, including tetralin,[26,28,52] 1-methyl-naphthalene,[20,24,25,29,52,60] CMNO,[49,60] light cycle oil,[22,49] heavy arenes,[20] NMP,[21,29] cyclohexane,[59] methanol,[31] and ethanol,[19,31] and the yields of soluble portions from thermal dissolution of lignites have a wide range of 8.0−88.1%, depending on the types of lignites and solvents as well as the temperature. Miura et al.[28,47] developed a flow-type reactor to separate organic matter in coals into soluble portions, enhancing the extract yields dramatically. Thermal dissolution of 15 lignites and subbituminous coals in CMNO and light cycle oil was performed to investigate the relationship between the yields of soluble portion and oxygen-containing functional groups.[49] When CMNO was used as solvent, the yield of the soluble portion increased linearly with decreasing quantity of carboxylate groups bridged by metal cations, such as Ca^{2+} and Mg^{2+}, and the intercept of the regression line (correlation coefficient is 0.82) between the yields of the soluble portion and the quantity of metal carboxylate groups is 57.8%. Koyano et al.[61] analyzed the data from yields of soluble portions in 1-methylnaphthalene at 360 °C and ultimate and proximate analyses for 76 lignites and bituminous coals. They found that the yield of the soluble portion could be successfully estimated by a multiple regression analysis (correlation coefficient is 0.79), and that a polar solvent, such as CMNO, is required to afford a higher yield of the soluble portion for coals with oxygen content more than 8.2%.

Although HyperCoal can be produced from different ranks of coals, the yield of HyperCoal from lignites is usually low due to the influence of hydrogen bonds and cross-linking interactions in lignites. By pretreating lignites with acid in addition to using a polar solvent,[29,49,62] the yield can be enhanced. Kashimura et al.[49] found that the yield (55.0%) of extract from Mulia lignite in CMNO is higher than (43.2%) that in light cycle oil, and pretreatment with 2-(2-methoxyethoxy)acetic acid also increased the extract yield when using CMNO as solvent. The enhancement of extract yield with polar solvents and acid pretreatment was ascribed to the relaxation of hydrogen bonds and breakage of cross-linking interactions, respectively.[49,53,62]

Lignites are known to decompose at lower temperature compared to higher-rank coals. Taking Loy Yang lignite as an example, 7% CO_2 formed at 350 °C owing to considerable decomposition of the lignite.[52] To reduce the formation of gaseous products, Ashida et al.[26,52] proposed a method of sequential thermal dissolution at different temperatures. Loy Yang lignite was subjected to sequential thermal dissolution in tetralin and 1-methylnaphthalene at 150−350 °C.[52] The results suggest that CO_2 formation was greatly suppressed during the sequential thermal dissolution process, presumably because smaller molecules were extracted at lower temperatures. Lu et al.[31] investigated sequential thermal dissolution of Huolinguole lignite at 200−330 °C in methanol and ethanol. As Figure 4 shows, once-through yields of methanol-soluble portions (MSPs) and ethanol-soluble portions (ESPs) appreciably decreased with raising temperature from 200 to 270 and 240 °C, respectively, but the ESP yields very rapidly increased, and the MSP yields remarkably increased with further raising the temperature. Significant increases in total yields of MSP and ESP also initiated from 270 and 240 °C and reached 23.0% and

Table 3. Yields of Soluble Portions from Thermal Dissolution of Lignites under Different Conditions

lignite	solvent	temperature (°C)	filtration approach	yield (%)	reference
Morwell	tetralin	325	hot	~20	Miura et al.,[28] 2001
Beulah Zap	1-methylnaphthalene	360	hot	28.8	Li et al.,[29] 2004
	NMP	360	hot	30.5	
Banko 97	1-methylnaphthalene	360	hot	30.6	
	NMP	360	hot	72.3	
Mulia	CMNO	360	hot	55.0	Kashimura et al.,[49] 2006
	light cycle oil	360	hot	43.2	
Loy Yang	tetralin	150−350[a]	hot	54	Ashida et al.,[26] 2008
Mulia	1-methylnaphthalene	300−400	hot	18.0−46.7	Takanohashi et al.,[25] 2008
Loy Yang	tetralin	150−350[a]	hot	56.8	Ashida et al.,[52] 2009
	1-methylnaphthalene	150−350[a]	hot	45.3	
Soma	NMP	202	room temperature	13.2	Sönmez et al.,[21] 2011
Çayırhan	NMP	202	room temperature	25.6	
Huolinguole	methanol	200−330[a]	room temperature	23.0	Lu et al.,[31] 2011
	ethanol	200−330[a]	room temperature	55.3	
Mequinenza	light cycle oil	360	hot	61.8	Kawashima et al.,[22] 2013
Xianfeng	1-methylnaphthalene	320	room temperature	17.1	Pan et al.,[24] 2013
BD	1-methylnaphthalene	400	hot	11.7	Rahman et al.,[20] 2013
	heavy arenes	400	hot	70.0	
BL	1-methylnaphthalene	400	hot	8.0	
	heavy arenes	400	hot	39.2	
Zhaotong	ethanol	305	room temperature	64.9	Li et al.,[19] 2014
Xianfeng	cyclohexane	200−320[a]	room temperature	11.0	Wang et al.,[59] 2015
Shengli	1-methylnaphthalene	360	room temperature	30.4	Shui et al.,[60] 2015
	CMNO	360	room temperature	42.3	
	1-methylnaphthalene + 15% ethanol	360	room temperature	81.8	
	CMNO + 15% ethanol	360	room temperature	88.1	

[a]Sequential thermal dissolution.

55.3% at 330 °C, respectively. At temperatures up to 240 °C, once-through yields of MSPs are appreciably higher than those of ESPs, whereas at temperatures higher than 270 °C, once-through yields of ESPs are drastically higher than those of MSPs. These results indicate that 270 and 240 °C could be initial temperatures for methanol- and ethanol-induced decomposition of Huolinguole lignite, respectively. In other words, thermal dissolution of Huolinguole lignite predominantly proceeded via dissociation of intermolecular interactions in Huolinguole lignite at temperatures lower than the corresponding initial temperature, but significant cleavage of covalent bonds in Huolinguole lignite proceeded at temperatures higher than the corresponding initial temperature. Most of the compounds detected in MSPs and ESPs with GC/MS are oxygen-containing species. MSPs are rich in methoxyarenes and methyl esters, while ESPs are rich in ethoxyarenes and ethyl esters. According to the distribution of oxygen-containing species, methanolysis and ethanolysis should be the main reactions during thermal dissolution of Huolinguole lignite. The alkanolysis mechanism was also proposed.[31] As Scheme 1 displays, as a nucleophilic atom in methanol or ethanol, oxygen can attack C_{aryl}, C_{acyl}, and/or C_{alkyl} and, subsequently, cleave the C_{aryl}−O, C_{acyl}−O, and/or C_{alkyl}−O bonds, resulting in the formation of phenols, alkoxyarenes, and esters.

Compared to Huolinguole lignite methanolysis at 310 °C, Shengli lignite methanolysis produced much more phenols, ketones, and alcohols but less arenes, alkanes, and esters; however, more than 50% of the MSPs from methanolysis of both Huolinguole and Shengli lignites are phenols (Table 4) and esters (Table 5).[63] Generally, phenols can be used to produce phenolic resins. The most popular phenolic resin is prepared from phenol and formaldehyde. Phenolic resins usually exhibit good adhesion properties, which make them suitable for use as a matrix of many organic and inorganic fillers and reinforcements. In addition, they are resistant to high temperatures and chemicals. Therefore, alkanolysis can be
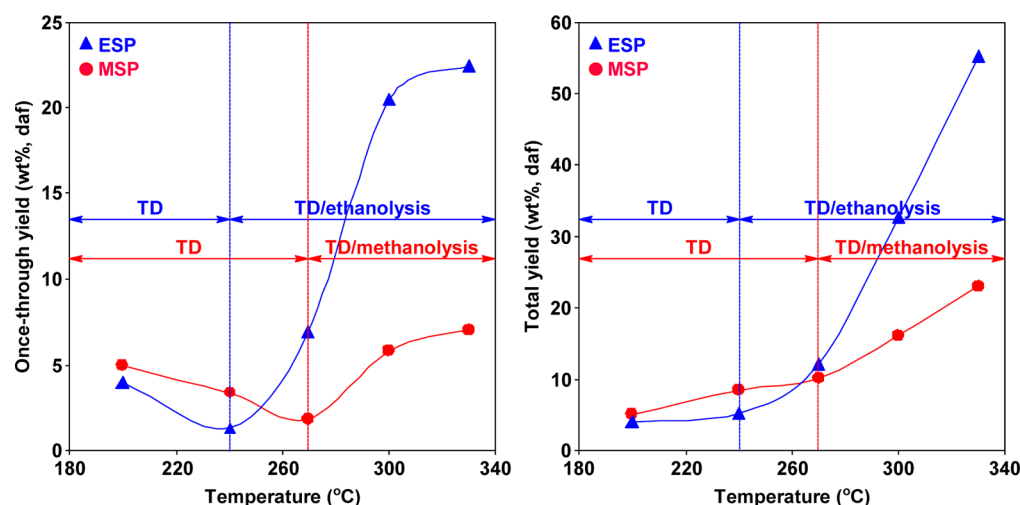
Figure 4. MSP and ESP yields from thermal dissolution (TD) of Huolinguole lignite at different temperatures. Adapted with permission from ref 31.

considered as a promising method for converting lignites into chemicals. Special attention should be paid to the consumption of methanol or ethanol during alkanolysis of lignites and separation and purification of the resulting products in the future. The alkanolyses of lignite-related model compounds, including benzyloxybenzene, anisole, phenethoxybenzene, and oxydibenzene, were simulated using density functional theory.[64] As a result, the alkanolyses involve nucleophilic attack, hydrogen transfer, and bond cleavage, and ethanolysis proceeds much more easily than methanolysis; e.g., the rate constant of benzyloxybenzene ethanolysis is 10 times more than that of benzyloxybenzene methanolysis at the same temperature. Reactivities of the lignite-related model compounds toward alkanolysis are benzyloxybenzene > anisole > phenethoxy-benzene > oxydibenzene. Isopropanol proved to be more effective than ethanol for coal alkanolysis due to the larger nucleophilicity of isopropanol than that of ethanol.[65]

Using thermal dissolution and subsequent column chroma-tography, a series of normal alkanes, polycyclic aromatics, methyl alkanoates, alkanoic acids, fatty acid amides,[66] and methyl alkanones[15] were enriched to large contents from thermally dissolved Shengli lignite. The polycyclic aromatics include three oxygen-containing species (3,5,7-trihydroxy-2-phenyl-4H-chromen-4-one, 9,10-dihydro-9,10,11-trimethyl-9,10-methanoanthracen-11-ol, and 1,2′-oxydinaphthalene), a nitrogen-containing compound (2,2′-biquinoline), and 11 condensed arenes (e.g., benzo[k]tetraphene, benzo[f]tetra-phene, and benzo[ghi]perylene). Condensed arenes are usually considered to be cancer-causing compounds.[67,68] On the other hand, they are also value-added chemicals in many applications, such as raw materials for synthesizing superior electrical conductive polymeric conductors,[69] organic dye molecules,[70] and narrow-band high-spin organic polymers.[71] However, synthesizing condensed arenes is an arduous and laborious work.[72,73] Compared to synthesis, enriching condensed arenes from coals and their derivates could be a more promising approach. Thus, further enriching and subsequently purifying the condensed arenes is an important subject. Additionally, 6-hydroxy-7-isopropyl-1,1,4a-trimethyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one was successfully isolated as a nearly pure compound from the thermally dissolved Shengli lignite.[66] The compound was reported to have anti-inflamma-tory activity[74] and not previously separated from any coal.

In recent decades, ionic liquids have been paid increasing attention in many fields due to their special physical-chemical characteristics, such as good chemical and thermal stability, unique dissolving capacity, and negligible vapor pressure.[75−78] Xianfeng lignite was subjected to thermal dissolution in a series of ionic liquids at 200 °C.[79] The results show that the anions in the imidazolium-based ionic liquids significantly affect the extract yield of Xianfeng lignite and the chemical characteristics of the extracts. Thermal dissolution of Xianfeng lignite in ionic liquids is related to the ability of ionic liquids to dissociate hydrogen bonds widely existing in lignites and 1-butyl-3-methylimidazolium chloride can dissociate almost all the hydrogen bonds in Xianfeng lignite. A comparative thermal dissolution of different coals in 1-butyl-3-methylimidazolium chloride shows that the extract yields of lignites are significantly higher than those of subbituminous coals and anthracites.[80] Compared to 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate, with lower melting point and viscosity, is more effective for thermal dissolution of Xianfeng and Shengli lignites.[81] The extract yield of Xianfeng lignite with 1-ethyl-3-methylimidazolium acetate reaches 93.0% at 200 °C for 0.5 h. The efficient recovery of ionic liquids from the ionic liquid/extract mixture is a challenge.

2.3. Application of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICRMS) in Analyzing Thermally Dissolved Portions from Lignites. Detailed analysis of molecular composition of soluble portions from thermal dissolution of coals is very important for efficiently utilizing the resulting soluble portions and challenging due to the highly complex compositions of the soluble portions. GC/MS has been successfully applied in identifying some species in coal extracts[33,82] and soluble portions from coal conversion,[83] but such identification is limited to relatively volatile, thermally stable, and less polar species. In addition, GC/MS analysis is easily affected by a complex matrix, and there are only limited standard libraries for the identification of detected species. FTICRMS proved to be a powerful tool for molecular characterization of extremely complex mixtures, such as petroleum,[84−87] coal-derived liquids,[19,88−96] and pyrolysis bio-oils.[97−99] It possesses an ultrahigh mass resolving power (>200,000) and mass accuracy (<1 ppm), allowing for baseline resolution of closely spaced isobaric species as well as distinct assignment of a unique elemental composition to each mass

Scheme 1. Possible Pathway of Huolinguole Lignite Alkanolysis
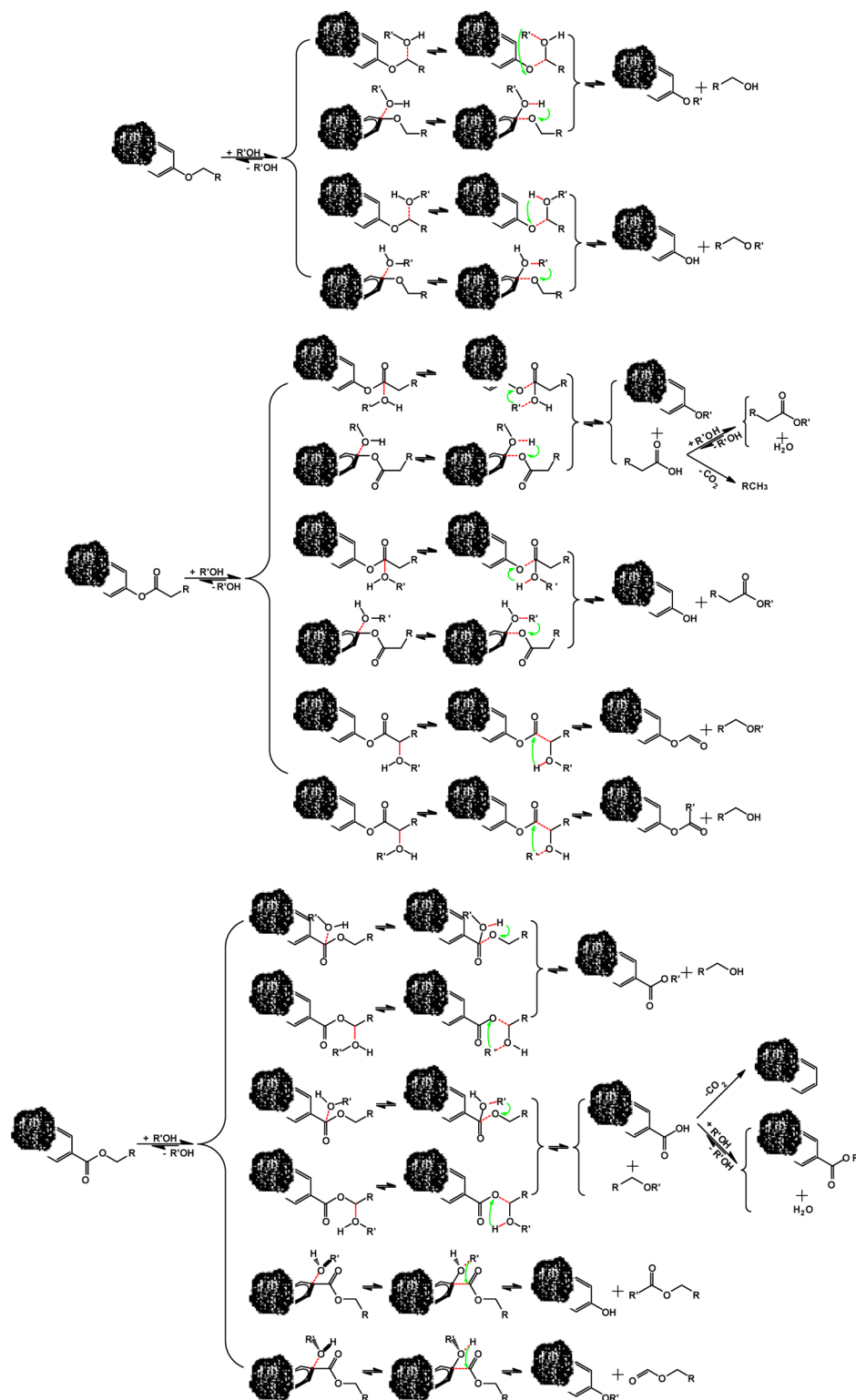
R denotes H, an alkyl, or and aryl group, and R' denotes a methyl or an ethyl group. Reprinted with permission from ref 31. Copyright 2011 American Chemical Society.

spectral peak. As a soft ionization technique, electrospray ionization (ESI) plays a critical role in the application of FTICRMS. ESI has a high selectivity for ionizing polar species in complex mixtures, avoiding time-consuming complex separation procedures. Each compositionally distinct component can be assigned to a definite "class" and "type" on the basis

of its heteroatomic number and double bond equivalent (DBE, rings plus double bonds) value.[100]

The ESP from Zhaotong lignite ethanolysis at 305 °C was analyzed with a 9.4 T ESI FTICRMS both in negative- and positive-ion modes for identifying oxygen-containing species and basic nitrogen compounds, respectively.[19,94] Such identi-

Table 4. Phenols Detected in MSPs from Shengli and Huolinguole Lignites[63]

no.	phenol	Shengli lignite	Huolinguole lignite
1	phenol	×	×
2	o-cresol	×	×
3	p-cresol	×	×
4	2-methoxyphenol	×	×
5	2,6-xylenol	×	×
6	2-ethylphenol	×	×
7	2,4-xylenol	×	×
8	4-ethylphenol	×	×
9	3-ethylphenol	×	×
10	3-methylguaiacol	×	
11	2,5-xylenol	×	×
12	2-ethyl-4-cresol	×	×
13	4-methoxy-3-cresol	×	×
14	4-methylguaiacol	×	×
15	mesitylenol	×	×
16	3-isopropylphenol	×	×
17	2,3,6-trimethylphenol	×	×
18	4-ethyl-3-cresol	×	×
19	2-ethyl-6-cresol	×	×
20	pseudocumene-1,4-diol	×	×
21	5-methoxy-2,3-xylenol		×
22	2-isopropyl-5-cresol	×	×
23	4-isopropylphenol	×	×
24	2-ethyl-4,5-xylenol	×	×
25	6-propyl-2-cresol		×
26	2,5-diethylphenol	×	
27	2,3,4,6-tetramethylphenol	×	×
28	2,3,5,6-tetramethylphenol	×	×
29	5-methoxyhemimellitenol	×	×
30	4-isopropyl-3-cresol	×	×
31	2-tert-butyl-4-methoxyphenol	×	×
32	2,6-diisopropylphenol	×	
33	4-methoxy-2,3,6-trimethylphenol	×	
34	2-(pent-3-en-2-yl)-4-cresol	×	×
35	2-(2-methylbut-3-en-2-yl)-3,6-xylenol	×	×

Table 5. Esters Detected in MSPs from Shengli and Huolinguole Lignites[63]

no.	ester	Shengli lignite	Huolinguole lignite
1	dimethyl succinate	×	
2	dimethyl glutarate	×	×
3	dimethyl 2-methylpentanedioate	×	
4	methyl 4-ethylbenzoate	×	×
5	dimethyl heptanedioate	×	×
6	methyl 3-methoxybenzoate	×	×
7	methyl 4-methoxybenzoate	×	×
8	4a-methyl-1,2,3,4,4a,5,6,7-octal-2-yl acetate	×	×
9	2,2-dimethylcyclohexyl acetate	×	
10	methyl undecanoate		×
11	dimethyl phthalate		×
12	methyl dodecanoate	×	×
13	dimethyl isophthalate		×
14	dimethyl nonanedioate		×
15	ethyl tridecanoate	×	×
16	dimethyl decanedioate	×	×
17	diisobutyl adipate	×	×
18	methyl 7-methylcyclopenta[c]pyran-4-carboxylate	×	×
19	methyl tetradecanoate	×	×
20	methyl 4-hydroxy-2-methoxy-3,5,6-trimethylbenzoate	×	×
21	methyl 1,1-dimethylindane-4-carboxylate	×	
22	methyl pentadecanoate	×	×
23	methyl 14-methylpentadecanoate		×
24	methyl palmitate	×	×
25	methyl heptadecanoate	×	×
26	methyl stearate	×	×
27	methyl octadeca-13,16-diynoate	×	
28	methyl nonadecanoate	×	×
29	methyl icosanoate	×	×
30	2-isopropyl-4b,8,8-trimethyl-4b,5,6,7,8,8a-hexahydrophenanthren-3-yl acetate	×	
31	methyl 7-isopropyl -1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate		×
32	methyl heneicosanoate	×	×
33	methyl docosanoate	×	×
34	methyl tricosanoate	×	×
35	methyl tetracosanoate	×	×
36	methyl pentacosanoate	×	×
37	methyl hexacosanoate	×	×
38	methyl heptacosanoate	×	×
39	methyl octacosanoate	×	×
40	methyl nonacosanoate	×	×

fication provides a good understanding of polar species in the ESP. In negative-ion mode,[19] most of the compounds detected in the ESP are oxygen-containing species of classes O_n and O_nN_1 ($n = 0-6$), especially O_1-O_4 class species with $1-12$ DBE values and $8-34$ carbon numbers. According to average DBE value, phenols, benzenepolyols, and benzoic acids with an aliphatic ring and alkyl chains are characteristic structures in the ESP. In positive-ion mode,[94] 86.4% of the detected species are basic nitrogen compounds, including N_1O_x ($x = 0-5$) and N_2O_y ($y = 0-2$) class species with $0-14$ DBE values and $9-39$ carbon numbers (Figure 5). On the basis of DBE distributions, pyridines and quinolines should be predominant basic nitrogen compounds in the ESP. Thermal- and solvent-induced destruction of noncovalent bonds in Zhaotong lignite could be responsible for the release of basic nitrogen compounds from the lignite. Sulfur-containing organic species in the soluble portion from thermal dissolution of Xianfeng lignite extraction residue in methanol were also analyzed with the ESI FTICRMS in negative-ion mode.[95] The results reveal that S_1O_x ($x = 0-5$), S_2O_x ($x = 0-5$), and N_3S_1 class species are the main sulfur-containing organic species in the soluble portion. Henicosane-1-thiol and alkylhydroxythiophenecarboxylic acids are domi-

nant in the S_1O_x class species. Sulfur in the S_2O_x class species is mainly present in thiol groups or S-heterocyclic rings (especially thiophene ring). Based on the understanding of the molecular composition of nitrogen- and sulfur-containing organic species in the soluble portion, thermal dissolution in methanol or ethanol and subsequent catalytic hydrodenitrogenation and hydrodesulfurization could be an optimum strategy for nitrogen and sulfur removal from lignites.

Although ESI FTICRMS has achieved success in identifying polar species in the soluble portions from thermal dissolution of lignites, it is not applicable for nonpolar and aprotic compounds, and the efficiency of ionization is usually poor for less poplar species as well.[87,100] To study the weekly polar compounds in the soluble portions from thermal dissolution of
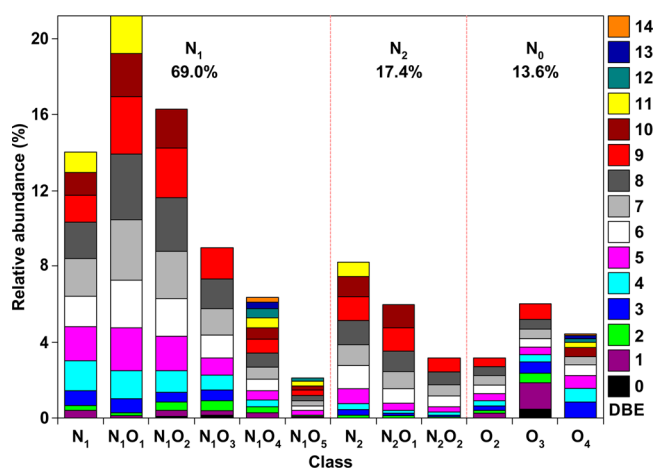
Figure 5. Relative abundances of N_xO_y class species in the ESP from Zhaotong lignite by positive-ion ESI FT-ICR MS analysis. Adapted with permission from ref 94.

lignites, further investigations are suggested to choose other ionization sources, such as atmospheric pressure photo-ionization source, atmospheric pressure solids analysis probe, and direct analysis in real-time source. Also, selective derivatization of functional groups will facilitate the sample ionization. In addition, using tandem/ion mobility mass spectrometry will help in identifying the structures of specific compounds.

3. LIGNITE OXIDATION UNDER MILD CONDITIONS

Many oxidants, such as O_2,[18,32,101−103] HNO_3,[104] H_2O_2,[1,17,24,105−108] NaOCl,[30,109−116] and RuO_4,[27,114,116−122] have been applied in coal oxidation under different conditions. Coal oxidation proved to be an effective approach for understanding coal structures and obtaining carboxylic acids. The typical carboxylic acids from coal oxidation include alkanoic acids, alkanedioic acids, alkanetricarboxylic acids, and BCAs (Figure 6). Most of them are important fine chemicals. For example, succinic acid can be used as a precursor for synthesizing many important industrial products, such as adipic acid, 1,4-butanediol, tetrahydrofuran, NMP, 2-pyrrolidinone, succinate salts, and γ-butyrolactone.[123] Adipic acid is the most important commercial aliphatic dicarboxylic acid, which is mainly used to produce nylon-66, polyurethane, and plasti-cizer.[124] Compared with the aliphatic carboxylic acids, BCAs are more value-added but more difficult to be obtained from the well-developed petrochemical industry. Phthalic acid and

terephthalic acid are the important feedstocks for plasticizers and polyesters, respectively. Trimesic acid is mainly used for producing the cross-linking agents of solid fuel as rocket boosters, alcohol−formaldehyde resins, water-soluble bakings, high-performance plastic plasticizers, and reverse-osmosis membranes for water desalination.[125] As a derivate of pyromellitic acid, pyromellitic dianhydride can be used to synthesize high-performance polyimides, plasticizers, curing agents for epoxy resin, alkyd resin coatings, and matting agents.[126] As a significantly useful polydentate ligand, mellitic acid demonstrates quite flexible ligand properties during the reaction with the metal ions to form complexes.[127]

3.1. Oxidation with Alkali-O_2. Coal oxidation with alkali-O_2 is a consecutive reaction, in which water-insoluble acids, water-soluble acids, BCAs, and CO_2 are sequentially produced with the trend of a decrease in molecular weight. In 1961, Kamiya[101] reported that water-soluble acids from a bituminous coal oxidation with alkali-O_2 were mainly 12 kinds of BCAs; the prospect of obtaining so many kinds of BCAs from coals was very exciting. Hayashi et al.[102] studied the oxidation of Yallourn and South Banko lignites with O_2 in the presence of Na_2CO_3 at 20−85 °C. They found that phenolic moieties are easily oxidized. Wang et al.[18] examined the effects of reaction parameters on BCA distribution from Huolinguole lignite oxidation with O_2 and NaOH and quantified the BCAs with high-performance liquid chromatography (HPLC). Their results show that BCAs with four or five carboxyl groups are the predominant products, and BCAs with one or two carboxyl groups are formed in a relatively short time. The oxidation behaviors of three lignites (Xiaolongtan, Huolinguole, and Shengli lignites) were compared, with an initial oxygen pressure of 5 MPa in the presence of an alkali at 240 °C.[32] In addition to the production of BCAs (18.4−21.5%), large amounts of lower fatty acids (39.8−23.2%), including oxalic acid, formic acid, acetic acid, succinic acid, and malonic acid, were obtained simultaneously. For the selected three lignites, the BCA yield slightly increases and lower fatty acid yield gradually decreases with increasing carbon content of the lignites. To understand the origin of lower fatty acids from lignite oxidation with alkali-O_2, the oxidation of lignite-related model compounds consisting of hexane, heptane, phenylpropane, fluorene, naphthalene, anthracene, phenanthrene, and 2-methyl-naphthalene was carried out under the same conditions.[32] The results suggest that lower fatty acids are mainly derived from the oxidation of aliphatic structures as well as the opening of benzene rings in lignites.
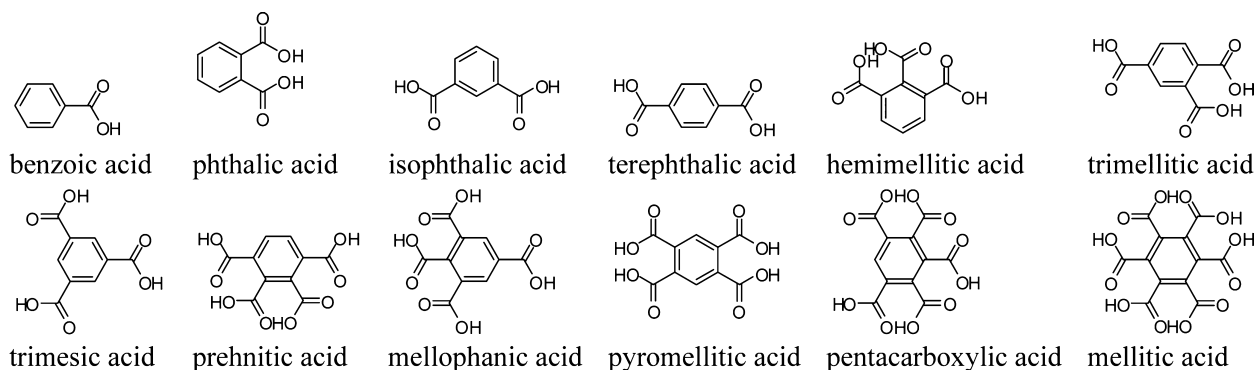

Figure 6. Structures of BCAs.

3.2. Oxidation with H_2O_2. Lignite oxidation with H_2O_2 was reported to be an effective method for producing lower fatty acids under mild conditions.[17] About 1 g of Beulah Zap lignite was oxidized with 20 mL of 30% H_2O_2 aqueous solution for 1–24 h at 40–80 °C.[17] Most of organic matter in the lignite was converted into water-soluble portion at 60 °C for 24 h and the water-soluble portion contains a large amount of lower fatty acids, such as formic acid, acetic acid, glycolic acid, and malonic acid. The water-soluble portion from the lignite oxidation with H_2O_2 was further oxidized with Fenton reagent at room temperature.[106] Through the two-step oxidation, 0.26 g/g-coal of lower fatty acids and 0.39 g/g-coal of BCAs were obtained from the lignite. According to the elemental balance before and after the oxidation, the mechanism for coal oxidation with H_2O_2 was proposed.[17] Fairly large amounts of hydrogen and oxygen, mainly as hydroxy radicals, were introduced from H_2O_2 to the macromolecules, leading to the formation of the small molecules. A series of heteroatom(s)-containing organic compounds were detected in water-soluble portion from Longkou lignite oxidation with H_2O_2 at 40 °C for 10 h.[107] Combining thermal dissolution with subsequent H_2O_2 oxidation, most of the organic matter in Xianfeng lignite was converted into soluble portion.[24] According to the analysis with a Fourier transform infrared (FTIR) spectrometer, the oxidation introduced carbonyl groups into the macromolecular matrix of Xianfeng lignite. The high yields of malonic and succinic acids and no benzenepolycarboxylic acids from the residue oxidation suggest that main bridged linkages between aromatic rings are $-CH_2-$ and $-CH_2CH_2-$, and benzene ring should be an important aromatic ring in Xianfeng lignite. Owing to intense oxidation and the release of a large amount of CO_2 at 80 °C, 5 g of extraction residue from Hulunbeier lignite was sequentially oxidized with 50 mL of H_2O_2 at 20–60 °C.[108] FTIR spectrometry analysis indicates that aromatic carbon content remained relatively unchanged at temperatures below 30 °C and slightly decreased with raising the oxidation temperature.

3.3. Oxidation with NaOCl. Chakrabartty and Kretschmer[109] first applied NaOCl to coal oxidation for characterizing coal structures. They speculated the presence of *n*-propyl and *n*-butyl groups in coals based on the detection of acetic and propionic acids in the resulting products. Mayo and Kirshen[112] found that coal oxidation with NaOCl was related to the alkalinity of aqueous solution. At pH 13, 80% of the dissolved carbonaceous species was present in high-molecular-weight acids, while at lower pH, more macro-molecular moieties in the coal were destroyed, resulting in the formation of fatty acids. Compared with H_2O_2, NaOCl has a higher reactivity toward oxidative degradation of coals and is more attractive for coal oxidation to produce carboxylic acids.[30,114−116,128] The oxidation behavior of Huolinguole lignite with NaOCl at 30 °C for 24 h was examined.[115] The resulting water-soluble portion was extracted with diethyl ether, carbon disulfide, petroleum ether, ethyl acetate, and benzene. According to GC/MS analysis, large amounts of chloro-substituted species were detected, and carboxylic acids were enriched into diethyl ether- and ethyl acetate-extractable portions, while carbon disulfide, petroleum ether, and benzene are effective for extracting normal alkanes. To explore the mechanism for coal oxidation with NaOCl, anthracene was used as a coal-related model compound and subjected to oxidation in aqueous NaOCl solution at 30–50 °C.[129] The results show that anthracene can be completely converted

within 48 h to produce 22 compounds. Non-chloro-substituted compounds are the main products and the mechanisms for anthracene oxidation and chlorination were reasonably proposed.[129] The addition of $O_2^{-\bullet}$ to 9-position in anthracene should be the initial and crucial step for anthracene oxidation. Many other coal-related model compounds (e.g., toluene, 2-methylnaphthalene, diphenylmethane, fluorene, benzyloxy-benzene, and indole) were also oxidized in aqueous NaOCl solution.[130] The results imply that the oxidation with NaOCl is complex and several reactions, such as addition, substitution, free radical formation, and oxidation, may simultaneously occur.

3.4. Difference in Oxidation with H_2O_2 and with NaOCl. A comparative study of Shengli lignite oxidation with H_2O_2 and NaOCl at 30 °C was conducted.[116] Most of the organic matter in Shengli lignite was converted into soluble portions in either H_2O_2 or NaOCl aqueous solution. The products from Shengli lignite oxidation with H_2O_2 are rich in hydroxy- and/or methoxy-substituted benzoic acids, alkanoic acids, and long-chain alkanedioic acids, whereas those from Shengli lignite oxidation with NaOCl mainly consist of BCAs, chloro-substituted short-chain alkanoic acids, and alkanedioic acids. The formation of large amounts of chloro-substituted species makes product separation and utilization difficult. Great efforts should be made to optimize the reaction conditions or develop new processes to minimize the formation of chloro-substituted species and increase the yields of valuable chemicals such as alkanoic acids, alkanedioic acids, and BCAs. The pretreatment with H_2O_2 proved to be an effective approach for promoting lignite oxidation with NaOCl. Shengli lignite was pretreated in H_2O_2 aqueous solution at 40 °C for 4 h and then oxidized in NaOCl aqueous solution at 30 °C for 5 h to investigate the effect of pretreatment on Shengli lignite oxidation with NaOCl.[30] As displayed in Figure 7 and Tables
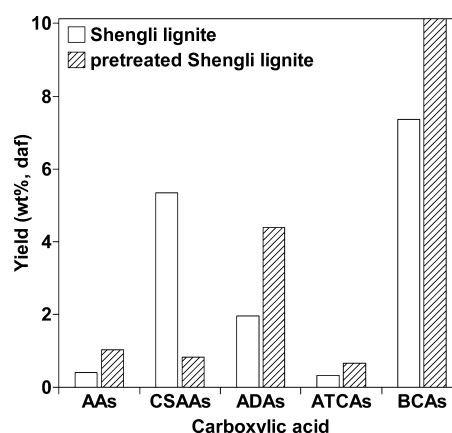

Figure 7. Distribution of different carboxylic acids from Shengli lignite NaOCl oxidation with and without H_2O_2 pretreatment. Adapted with permission from ref 30. Abbreviations: AAs, alkanolic acids; CSAAs, chloro-substituted alkanoic acids; ADAs, alkanedioic acids; ATCAs, and alkanetricarboxylic acids.

6 and 7, the pretreatment with H_2O_2 significantly increases the yields of alkanoic acids, alkanedioic acids, and BCAs, and substantially suppressed the formation of chloro-substituted alkanoic acids. Direct analysis in real-time ionization source coupled to an ion trap mass spectrometer analysis exhibits that the pretreatment with H_2O_2 enhances the formation of compounds with m/z 300−500. The increase in the yields of soluble species could be ascribed to the cleavage of covalent

Table 6. Yields (mg·g^{-1}, daf) of Chloro-Substituted Alkanoic Acids and Alkanedioic Acids from Shengli Lignite and H$_2$O$_2$-Pretreated Shengli Lignite Oxidation in NaOCl[30]

no.	compound	yield from Shengli lignite	yield from pretreated Shengli lignite
1	chloroacetic acid	0.4	0.2
2	2-chloropropanoic acid	0.1	0.1
3	2-chloroacrylic acid	<0.1	0.1
4	dichloroacetic acid	10.8	1.8
5	2,2-dichloropropanoic acid	0.6	
6	trichloroacetic acid	13.8	3.3
7	2,3-dichloroacrylic acid	0.5	
8	2-chloro-3-hydroxybutanoic acid	0.2	0.3
9	2,2-dichlorobutanoic acid	0.5	
10	2,3,3-trichloroacrylic acid	1.2	0.9
11	2,2-dichloropentanoic acid	17.0	
12	2,2,3,3-tetrachloropropanoic acid	7.1	1.6
13	2,2,3,3,3-pentachloropropanoic acid	1.3	
14	oxalic acid	0.2	0.2
15	fumaric acid	0.6	1.5
16	succinic acid	6.1	7.9
17	2-methylsuccinic acid	2.3	3.5
18	2,3-dimethylsuccinic acid		0.2
19	glutaric acid	0.7	0.5
20	4-(1-carboxyethoxy)butanoic acid		11.2
21	2-ethylsuccinic acid		2.8
22	2-methyloxirane-2,3-dicarboxylic acid	0.3	0.1
23	3-methylglutaric acid	0.1	0.4
24	3-(carboxymethyl)oxirane-2-carboxylic acid	1.3	0.2
25	2-oxoglutaric acid		1.6
26	2-isopropylsuccinic acid		0.3
27	3-hydroxy-2-methylglutaric acid		0.5
28	3-oxoheptanedioic acid		0.3
29	adipic acid	0.4	0.6
30	2-methyladipic acid		0.2
31	2-chloropentanedioic acid		0.2
32	3-methyladipic acid		0.4
33	4-(1-carboxyethoxy)butanoic acid		1.8
34	4-methylheptanedioic acid	0.1	0.1
35	octanedioic acid	0.4	0.6
36	2,3-dimethylfumaric acid		0.7
37	2-ethylidenesuccinic acid		0.7
38	2-chloro-3-(dichloromethyl)fumaric acid	5.3	5.5
39	nonanedioic acid	0.3	0.8
40	4-oxohept-2-enedioic acid	1.5	
41	decanedioic acid		0.6
42	undecanedioic acid		0.5

bonds and introduction of oxygen-containing functional groups such as −COOH and −OH into Shengli lignite by the pretreatment with H$_2$O$_2$.

In summary, H$_2$O$_2$ and NaOCl are also suitable industrial oxidants for producing carboxylic acids from lignites in addition to O$_2$ because of their low price, availability, and eco-friendliness. The optimization of reaction conditions such as the ratio of an oxidant to a lignite, reaction temperature, and reaction time still needs to be investigated to reduce side reactions, especially chlorination. In addition, more efforts should be made to investigate the mechanism, kinetics, and selectivity of lignite oxidation for producing value-added chemicals. For instance, simulations using density functional theory can also be applied in the elucidation of oxidation mechanism.

3.5. Ruthenium Ion-Catalyzed Oxidation (RICO). RICO was first reported to be an effective method for selective elimination of aromatic rings in 1953,[131] and since then this approach has been widely used for characterizing structures of coals and their derivates.[27,116−121,132] Detailed analysis of the products from the RICO of Yallourn and South Banko lignites was performed by field desorption mass spectrometry and ^{13}C nuclear magnetic resonance spectroscopy.[27] The results indicate that water-soluble portions consist of alkanedioic acids and BCAs with long alkyl side chains and organic phases contain a large amount of alkanoic acids with long alkyl groups up to C$_{38}$. Extensive investigations[133−135] have been performed on the mechanisms for the oxidation of coals and their related model compounds with RuO$_4$. It is usually accepted that RuO$_4$ selectively oxidizes aromatic ring-containing species to carboxylic acids, including alkanoic acids, alkanedioic acids,

Table 7. Yields (mg·g^{-1}, daf) of BCAs from Shengli Lignite and H$_2$O$_2$-Pretreated Shengli Lignite Oxidation in NaOCl[30]

no.	BCA	yield from Shengli lignite	yield from pretreated Shengli lignite
1	benzoic acid	0.2	0.4
2	4-methoxybenzoic acid	0.8	1.2
3	3-methoxybenzoic acid		0.4
4	2-fluoroterephthalic acid	3.2	1.1
5	3-chlorobenzoic acid	0.2	0.4
6	2-chlorobenzoic acid		0.4
7	phthalic acid	3.7	4.7
8	terephthalic acid	0.4	1.1
9	isophthalic acid	1.3	2.7
10	4-chlorophthalic acid	0.5	2.0
11	3,5-dichloro-4-methoxybenzoic acid		0.9
12	2-chloroterephthalic acid		0.8
13	chloromethylphthalic acid	1.3	1.5
14	5-chloro-3,4-dimethylphthalic acid		0.4
15	hemimellitic acid	6	8.3
16	trimellitic acid	13.3	23.6
17	trimesic acid	0.9	1.8
18	chlorobenzenetricarboxylic acids		3.5
19	toluenetricarboxylic acids	1.8	0.1
20	chloromethylbenzenetricarboxylic acids	4.0	8.9
21	prehnitic acid	8.2	5.7
22	pyromellitic acid	12.4	10.2
23	mellophanic acid	8.8	15.2
24	chlorobenzenetetracarboxylic acids	0.2	0.5
25	chloromethylbenzenetetracarboxylic acids	1.7	0.7
26	2-acetyl-5-(1-hydroxyvinyl)-3-methylterephthalic acid		0.2
27	benzenepentacarboxylic acid	3.2	3.1
28	6-toluene-1,2,3,4,5-pentacarboxylic acid	0.2	0.7
29	6-chlorobenzene-1,2,3,4,5-pentacarboxylic acid	0.1	0.2
30	mellitic acid	1.2	0.5

and BCAs, as shown in Scheme 2. Consequently, the compositional analysis of the resulting carboxylic acids from

Scheme 2. RICO Mechanisms of Alkylbenzene, 1,3-Diphenylpropane, and Anthracene
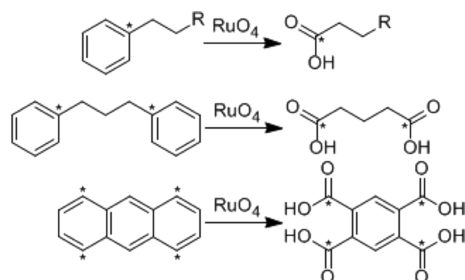
lignite RICO can offer the information about the distribution of side chain groups and bridged linkages in lignites.

Structural features of macromolecular aromatic species in Huolinguole lignite were examined through RICO.[120] GC/MS analysis of the resulting soluble species shows that alkanedioic acids are predominantly abundant (Figure 8a) and most of them are succinic acid and glutaric acid (Figure 8b), implying
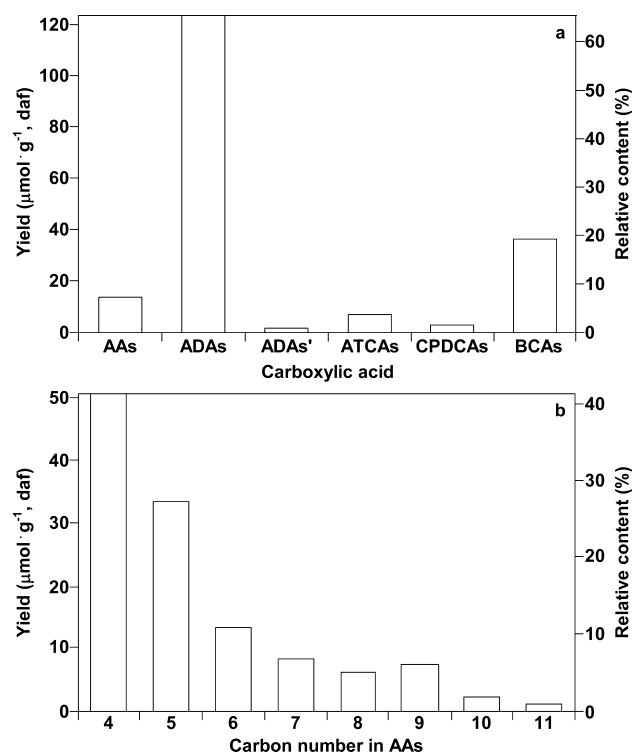
Figure 8. Distribution of different carboxylic acids (a) and carbon number in AAs (b) from RICO of Huolinguole lignite. Adapted with permission from ref 120. Abbreviations: AAs, alkanolic acids; ADAs and ADAs′, alkenedioic acids; ATCAs, alkanetricarboxylic acids; CPDCAs, cyclopentanedicarboxylic acids.

that Huolinguole lignite is rich in bridged linkages and −CH$_2$CH$_2$− and −CH$_2$CH$_2$CH$_2$− are the main bridged linkages connecting aromatic rings. According to the analysis with an atmospheric pressure solid analysis probe/time-of-flight mass spectrometer, small amounts of biphenylpolycarboxylic acids, alkylbiphenylpolycarboxylic acids, and alkylphenylnaphthalenepolycarboxylic acids with 6−10 carboxylic groups and C$_1$−C$_4$ alkyl groups were produced from RICO of Huolinguole lignite, suggesting that highly condensed aromatic species in Huolinguole lignite contain biphenyl and phenylnaphthalene skeleton structures. Extraction residues from supercritical methanolysis of Huolinguole and Shengli lignites were also subjected to RICO.[119] The results demonstrate that the extraction residue from Shengli lignite is richer in highly condensed aromatic species than that from Huolinguole lignite, while both extraction residues have the same distribution of alkylene bridges (C$_2$−C$_{20}$) connecting aromatic rings with a higher abundance of shorter linkages than that of longer linkages. Understanding such abundant short alkylene bridges facilitates directional conversion of lignites, i.e., a smart process can be developed to catalytically hydrocrack Ar−CH$_2$−Ar′ bonds at low temperatures under pressurized hydrogen and thermally break ArCH$_2$−CH$_2$Ar′ bonds at elevated temperatures under low pressure. Although the selectivity is excellent, RICO for coals has not been well developed due to the high cost of RuO$_4$.

3.6. Separation of BCAs. Owing to similar properties and very low volatility, separating BCAs from lignite oxidation is difficult. Various methods, such as supercritical fluid chromatography,[136] HPLC,[137,138] and use of deep eutectic solvents,[139] have been applied to separate BCAs. Berger and Deye[136]

investigated the separation of BCAs by packed column supercritical fluid chromatography using methanol/carbon dioxide mixtures with very polar additives. Without the additive, few of BCAs can be eluted and peak shapes tend to be poor, while BCAs could be efficiently separated using only modest concentrations of additives. Kawamura et al.[137] used reversed-phase HPLC with quaternary ammonium salts to separate BCAs. They discussed the retention mechanism of BCAs on the basis of both ion-pair partition and ion-exchange models. BCAs with one carboxylic group mainly follow ion-pair partition model and BCAs with multiple carboxylic groups primarily follow ion-exchange mechanism. This approach was also applied for the analysis of products from Loy Yang lignite oxidation with alkali-O_2.[138] It was confirmed that the results obtained using this method are consistent with those determined using GC. Recently, quaternary ammonium salts were reported to be effective for separating BCAs via the formation of deep eutectic solvents.[139] Among the selected three quaternary ammonium salts (choline chloride, tetramethylammonium chloride, and tetraethylammonium chloride), tetraethylammonium chloride was found to have the best performance, completely separating BCA isomers in butanone. The formation of hydrogen bonds between quaternary ammonium salts and BCAs is responsible for the selective separation of BCAs. Additionally, quaternary ammonium salt in deep eutectic solvent could be effectively recovered by the antisolvent method of isopronol. Although such methods have been successfully applied in separating BCAs, further efforts are needed to optimize the separation processes, making them cost-effective and practical.

4. CATALYTIC HYDROCONVERSION OF LIGNITES UNDER MILD CONDITIONS

Catalytic hydroconversion includes catalytic hydrogenation, hydrocracking, hydrodenitrogenation, hydrodeoxygenation, and hydrodesulfurization. Developing highly active catalysts is crucially important for lignite hydroconversion under mild conditions. Because of the high complexity of coal structures, studies on the reactions of coal-related model compounds have become powerful tools to reveal the mechanism of coal liquefaction on the molecular level. Previous investigations with coal-related model compounds indicate that metals catalyze biatomic hydrogen transfer, resulting in the hydrogenation of unsaturated moieties, especially aromatic rings,[140,141] while metal sulfides[140−144] and activated carbon[145−147] facilitate monatomic hydrogen transfer, i.e., radical hydrogen transfer, and solid acids promote proton transfer,[148] leading to the cleavage of some covalent bonds, especially strong bridge bonds, e.g., Ar−X−Ar′ bonds (Ar and Ar′ denote aromatic rings and X denotes CH_2, O, S, or NH).

4.1. Metal-Based Catalysts. Iron-based catalysts, especially iron sulfides, are well-known to be the most practical catalysts for coal liquefaction because of their low cost and environmentally benign for disposal.[149−154] It is widely believed that $Fe_{1−x}S$ is an active phase for iron sulfides during coal liquefaction,[155−157] but in fact the formation of $H^{\bullet}$ during the reactions of H_2 with FeS_2-derived radicals such as sulfur biradicals and $HS^{\bullet}$ plays a crucial role in coal liquefaction according to the investigations of model reactions.[140−143] The comparison of activities of FeS, FeS+S, and SO_4^{2-}/ZrO_2 for the hydroconversion of Xiaolongtan lignite shows that FeS+S is more effective than the other two catalysts.[158] Adding sulfur and increasing initial hydrogen pressure favor the formation of

active hydrogen over FeS+S for breaking some strong bridged bonds, hydrogenating condensed aromatic rings, and stabilizing free radicals produced from thermal cleavage of weak bridged bonds to form more light species. Kaneko et al.[149] examined the effect of a highly dispersed γ-FeOOH on hydroconversion of Yallourn lignite. The catalyst was prepared by coprecipitation of aqueous ferrous sulfate and ammonia and subsequent oxidation with O_2. It has a much higher specific surface area (67 m^2/g) than natural pyrite (15 m^2/g). Compared with the conventional pyrite, consumption of hydrogen during the lignite hydroconversion significantly increased over γ-FeOOH. Li et al.[152] studied the role of Na_2CO_3 in Shengli lignite hydroconversion with γ-FeOOH/α-FeOOH at 400 °C. They found that Na_2CO_3 and Fe-based catalysts exhibit a synergic effect on increasing the oil yield and reducing water production from Shengli lignite. The synergic effect is mainly attributed to the promotional role of Na_2CO_3 in the depolymerization of macromolecules and hydrolyzation of oxygen-containing moieties in lignites.

In addition to iron, other metals such as molybdenum,[159−161] nickel,[160,162−164] and cobalt[160,165] were also used to lignite hydroconversion. Among them, molybdenum-based catalysts have attracted much attention due to the effectiveness of well dispersed molybdenum at low concentrations and the function of removing heteroatoms.[166,167] Hulston et al.[160] reported that pretreatment with nickel acetate/ammonium molybdate is more effective than that with cobalt acetate/ammonium molybdate for hydroconversion of Loy Yang lignite at 400 °C. Addition of carbon disulfide as sulfur source could eliminate the difference between the two catalysts, but neither is more active than a molybdenum sulfide. The hydrogenation of aromatic rings is inevitable in addition to the release of hydrogen sulfide over metal sulfides, although the total selectivity of hydrogenated products was very low from the reaction of diphenylmethane.[142]

The hydrocracking of bridged C−O bonds in lignites is important for lignite degradation. In our recent investigation,[164] using $Ni(CO)_4$ as precursor, a highly active Ni/mesoporous attapulgite was prepared for hydrocracking C−O bonds. Benzyloxybenzene was used as a lignite-related mode compound to evaluate the catalyst activity for C−O bond cleavage. The result indicates that benzyloxybenzene was completely converted to toluene and phenol under pressurized hydrogen at 150 °C over the catalyst. The catalyst has been successfully applied to hydroconversion of rice straw and is also expected to be effective for hydroconversion of lignites and their derived liquids.

4.2. Acid Catalysts. Although liquid or soluble acids such as $ZnCl_2$,[161] $SnCl_2$,[161] HF−BF_3,[168,169] and CF_3SO_3H[170] proved to be effective for coal liquefaction, they are corrosive and cannot be effectively recovered, which limits their utilization in commercial process. Since solid acids have the advantages of low corrosion and good retrievability, increasing attention is paid to develop solid acids for coal liquefaction.

Three solid acids were prepared by impregnating the same volume of pentachloroantimony, trimethylsilyl trifluoromethanesulfonate, or isometric pentachloroantimony and trimethylsilyl trifluoromethanesulfonate into an activated carbon. Di(1-naphthyl)methane was used as a coal-related model compound to evaluate their catalytic activity.[148] The results exhibit that $C_{ar}−C_{alk}$ bond in di(1-naphthyl)methane can be specifically cleaved over each catalyst to afford naphthalene and 1-methylnaphthalene under pressurized hydrogen at temperatures up to 300 °C, while as a new solid

acid (NSA), pentachloroantimony-trimethylsilyl trifluoromethanesulfonate/activated carbon is obviously more active for di(1-naphthyl)methane hydrocracking than the other two solid acids. As illustrated in Figure 9, di(1-naphthyl)methane
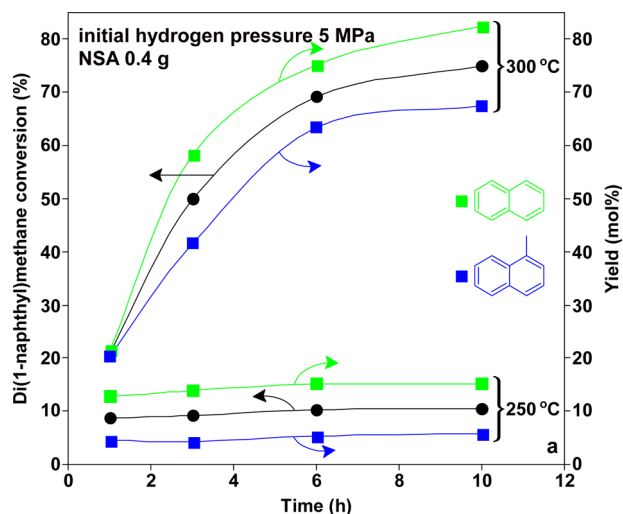

Figure 9. Time profiles of di(1-naphthyl)methane conversion and product yield at 250 and 300 °C. Adapted with permission from ref 148.

hydrocracking significantly proceeds at 300 °C and di(1-naphthyl)methane conversion increases with raising temperature and prolonging time. Interestingly, the yield of naphthalene is remarkably higher than that of 1-methylnaphthalene, indicating that demethylation of 1-methylnaphthalene also proceeds. As exhibited in Scheme 3, H_2 could be heterolytically dissociated to immobile H^- and mobile H^+. The addition of mobile H^+ to *ipso*-position of di(1-naphthyl)methane should be crucial step for di(1-naphthyl)methane hydrocracking. The high activity of NSA for the specific cleavage of bridged bond in di(1-naphthyl)methane could be ascribed to the catalysis of NSA in effective producing immobile H^- and mobile H^+.

The NSA was used to hydroconversion of Shengli lignite in cyclohexane at 300 °C for 3 h under 5 MPa of initial hydrogen pressure.[171] The reaction mixtures from both noncatalytic hydroconversion and catalytic hydroconversion 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 the total extract yield from catalytic hydroconversion

exceeded 60% of organic matter in Shengli lignite and is appreciably higher than that from noncatalytic hydroconversion of Shengli lignite. All the extracts were analyzed with GC/MS, but GC/MS-detectable species only appeared in E_1 from noncatalytic hydroconversion and catalytic hydroconversion of Shengli lignite, implying that the GC/MS-detectable species were exhaustively extracted by petroleum ether. E_1 mainly consists of alkanes, arenes, and oxygen-containing species, and most of the arenes are methyl-substituted ones; most of the oxygen-containing species are arenols, especially alkylarenols. All the yields of alkanes, arenes, and arenols from catalytic hydroconversion are obviously higher than those from noncatalytic hydroconversion of Shengli lignite. Alkylarenes and alkylarenols may be released by the addition of catalytically formed H^+ over the NSA to the *ipso*-position of condensed aromatic rings in Shengli lignite.

5. CONCLUSIONS

Fractional extraction and subsequent column chromatography are effective for enriching and isolating many organic compounds from lignites. The yields of soluble portions from thermal dissolution of lignites range widely from 8.0% to 88.1%, depending on the types of lignites and solvents. Polar industrial solvents such as CMNO are suitable for preparing HyperCoals from lignites. Additionally, alkanols, especially methanol and ethanol, proved to be effective for thermal dissolution of lignites, and alkanolysis proceeds during the thermal dissolution process, along with the formation of large amounts of phenols and esters. Oxidative depolymerization of lignites provides a potential approach for producing carboxylic acids. Extraction, thermal dissolution, mild oxidation, and catalytic hydroconversion should be integrated for efficiently degrading lignites. Large-scale conversion of lignites under mild conditions needs further investigation, including a techno-economic analysis of the aforementioned processes, optimal preparation of highly active and renewable superacid and superbase catalysts, and development of technologies for highly selective oxidation of lignites and effective separation of the resulting products.
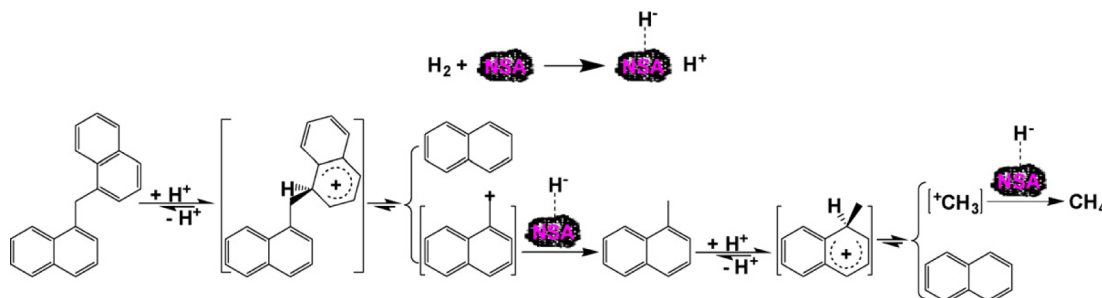
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Notes

The authors declare no competing financial interest.

Scheme 3. Possible Mechanism for the NSA-Catalyzed Hydrogen Transfer to Di(1-naphthyl)methane

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■ NOMENCLATURE

BCAs = benzenecarboxylic acids
CMNO = crude methylnaphthalene oil
DBE = double bond equivalent
ESI = electrospray ionization
ESPs = ethanol-soluble portions
FTICRMS = Fourier transform ion cyclotron resonance mass spectrometry
FTIR = Fourier transform infrared
GC/MS = gas chromatograph/mass spectrometer
HPLC = high-performance liquid chromatography
MSPs = methanol-soluble portions
NMP = N-methyl-2-pyrrolidinone
NSA = new solid acid
RICO = ruthenium ion-catalyzed oxidation

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