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Full Length Article

Mild oxidation of Yanshan petroleum coke with aqueous sodium hypochlorite

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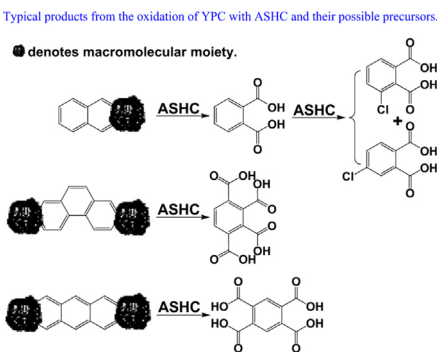
GRAPHICAL ABSTRACT

Typical products from the oxidation of YPC with ASHC and their possible precursors.



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ABSTRACT

Yanshan petroleum coke (YPC) was subjected to oxidation with aqueous sodium hypochlorite under mild conditions followed by subsequent solvent extraction to afford various arenecarboxylic acids (ACAs). In total, 77 compounds were identified with a chromatograph/mass spectrometer, which can be classified into 14 group components. Among them, benzenepolycarboxylic acids (BPCAs) are the most abundant. The results indicate that YPC is rich in condensed aromatic moieties. The formation of $O_2^{-\cdot}$ is vital to the decomposition of the condensed aromatic moieties in YPC to ACAs. Chlorine-containing BPCAs with more than 2 carboxylic groups were not detected, manifesting that ACA chlorination proceeded *via* Cl_2 addition and subsequent HCl elimination rather than $Cl^{\cdot}$ substitution. BPCAs and heavier ACAs were produced from condensed aromatics and substituted arenes, respectively, in YPC. Benzenecarboxylic acids (BCAs) and their chlorides can be enriched into different fractions by solvent extraction, facilitating the YPC utilization as a chemical resource. Hence, this investigation provides a promising approach for obtaining BCAs, especially BPCAs, from YPC and for understanding aromatic structural features in organic matter of YPC.

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Nomenclature

ACAs	arenecarboxylic acids
ADAs	alkanedioic acids
AHs	anhydrides
AHMS	anhydrous magnesium sulfate
AHSS	anhydrous sodium sulfite
ASHC	aqueous sodium hypochlorite
BCAs	benzenecarboxylic acids
BPCAs	benzenepolycarboxylic acids
BPCAs'	biphenylcarboxylic acids
CAs	carboxylic acids
CAs'	condensed aromatics
CARs	condensed aromatic rings
CCAAs	chlorine-containing alkanoic acids
CCBCAs	chlorine-containing benzenecarboxylic acids
CD	condensation degree
CG	carboxy group
CGN	carboxy group number
CSACAs	chlorine-substituted ACAs
DCTMNAs	6,7-dichlorotetramethyl-2-naphthoic acids
DMACAs	dimethylanthracenecarboxylic acids
EA	ethyl acetate
EOE	ethoxyethane
ES_{1-2}	extraction solution 1–2
F_{1-2}	filtrate 1–2
FC_{1-2}	filter cake 1–2
GC/MS	gas chromatograph/mass spectrometer
HACAs	heavier arenecarboxylic acids
IES_{1-2}	inextractable solution 1–2
MBCAs	methylbenzenecarboxylic acids
MEE_{1-2}	methyl esterified extract 1–2
$MEIEF_2$	methyl esterified inextractable fraction 2
MMMs	macromolecular moieties
MMPs	macromolecular precursors
NCAs	naphthalenecarboxylic acids
NCACAs	non-chlorine ACAs
NSBCAs	non-substituted benzenecarboxylic acids
OSs	other species
PA	phthalic acid
PCs	petroleum cokes
PMNAs	polymethyl-2-naphthoic acids
PMNDCAs	polymethylnaphthalene-2,3-dicarboxylic acids
PMNPCA s	polymethylnaphthalenetpolycarboxylic acids
PNCAs	phenylnaphthalenecarboxylic acids
RC	relative content
TRC	total relative content
TY	total yield
YPC	Yanshan petroleum coke

1. Introduction

Petroleum cokes (PCs), as the by-products in the oil refining process, have a continuously increasing output with the industrialization process of China, because *ca.* 31 kg PCs are produced from 1 t crude oil [1,2]. Recently, many attempts have been tried to utilize PCs effectively. Due to the low price, high carbon content and calorific value (*ca.* 33.5 $MJ \cdot kg^{-1}$), low ash content (< 4%), and easy availability, PCs are used as attractive raw materials for aluminum smelting industries, cement industries, power generation industries, graphite electrodes for steel production, and nonferrous industries [3,4]. However, the quality deterioration of crude oil leads to the concentration of environmentally harmful elements, primarily sulfur, and toxic elements, such as Ni and V, which can catalyze oxidation reactions, leading to higher consumption of carbon in the electrolysis cell. Low quality PCs cannot meet relevant industry production need and are usually regarded as fuels. Key concerns with the combustion of PCs are SO_x emission, causing serious environmental problems and the toxicity of V_2O_5 formed and released during combustion [1,5,6]. Therefore, it is necessary to develop a novel conversion method to utilize PCs effectively and reasonably.

PCs are rich in highly condensed aromatics (CAs') with thermal stability. Thus, pyrolyzing PCs requires higher energy and rigorous conditions, such as high temperatures, which are essential in the application processes mentioned above, leading to extra costs and equipment impacts. Hence, a mild conversion process is more promising for efficiently utilizing PCs. On the other hand, many aromatics, especially CAs', are value-added chemicals, which are widely used to produce nano-optoelectronic devices and solar cell [7,8]. Hence, using PCs as raw materials for obtaining fine organic chemicals is more promising than producing fuels.

Coal oxidation provides an effective method for obtaining carboxylic acids (CAs) and understanding coal structures at the molecular level. Insoluble species in coals can be converted to soluble alkanoic acids, alkanedioic acids (ADAs), and arenepolycarboxylic acids (ADAs) *via* oxidation under mild conditions [9–17]. The resulting CAs are useful for synthesizing functional materials [18], medicines [19], and aircraft fuels [20]. Moreover, environmental pollutants, such as SO_x and V_2O_5, will not be released in the oxidation process. Therefore, oxidation satisfies the requirements for efficient and clean utilization of PCs.

Many oxidants, such as O_2, H_2O_2, and RuO_4, have been applied in coal oxidation [21]. Due to the low price, easy availability, and eco-friendliness, NaOCl has great potential to produce CAs in industry. Most of organic matter in Shenfu subbituminous coal was converted to soluble species *via* oxidation with NaOCl [22]. Benzenehexacarboxylic acid can be concentrated over 34% by sequentially oxidizing Jincheng No. 15 anthracite and subsequent solvent extraction [23]. However, to the best of our knowledge, few reports have been issued on the mild oxidation of PCs with NaOCl.

PCs have highly condensed aromatic moieties similar to high-rank coals, so oxidation with NaOCl should also be a promising approach for obtaining CAs and investigating structural features of PCs. The conversion conditions are mild and PCs are used as precursors value-added chemicals rather than raw materials or fuels. Taking this expectation into account, in the present study, Yanshan petroleum coke (YPC) was subjected to oxidation with NaOCl to explore the structural features of YPC and speculate the possible mechanism for the formation of CAs from the oxidation.

2. Experimental

2.1. Materials

YPC was taken from Sinopec Beijing Yanshan Company and pulverized to pass through a 200-mesh sieve followed by desiccation in a vacuum at 80 °C for 24 h prior to use. The proximate and ultimate analyses of YPC were listed in Table 1. Ethoxyethane (EOE), ethyl acetate (EA), aqueous HCl (36%), aqueous sodium hypochlorite (ASHC) (6% available chlorine), anhydrous sodium sulfite (AHSS), and anhydrous magnesium sulfate (AHMS) used in the experiments are analytical reagents and all the organic solvents were distilled before use.

2.2. YPC oxidation with ASHC

As illustrated in Fig. 1, YPC (1 g) and ASHC (150 mL) were added