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A temperature-programmed oxidation method for quantitative characterization of the thermal cokes morphology

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HIGHLIGHTS

- TPO has high sensitivity to variation in terms of carbon species and order.
- Heat peaks representing different carbon species have been defined.
- TPO is a convenient method to quantitatively study the morphology of coke.

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ABSTRACT

A series of thermal cokes obtained by coking of vacuum residues and fractions have been studied by polarized light microscopy observation, scanning electron microscope (SEM), and temperature-programmed oxidation (TPO) technique. The anisotropic degrees of coke samples are found to be considerably different for discriminating characterization, which indicates that the coke morphology is closely dependent on the chemical nature of the coking materials. The restricted mesophase development in thermal coke might be ascribed to the increasing amount of heteroatoms contained in the parent coking materials. A proper signal analysis procedure of TPO profiles was obtained to discriminate the carbon species in the coke quantitatively, and then a good one-to-one correlation between determinations by polarized-light micrographs analysis and TPO method was observed, which shows that the TPO technique could be a suitable and more rapid method than polarized-light microscopy to quantitatively assess the morphology of coke, even in some situations in which the traditional method is inadequate.

1. Introduction

The quantitative assessment of the thermal coke morphology is necessarily important for the understanding of the reactivity [1] and the structural characterization of thermal coke [2–4], which could determinate the final utilization of coke, such as serving as a type of solid fuel in the pulverized furnace [5], or being a filler material of electrodes for aluminum manufacture [6]. The identification and characterization of thermal coke morphology are typically investigated using polarized light optical microscopy observation with various image analysis methods to determine the general morphology, particle size, degree of anisotropy [2,6–8], etc. However, quantitative determination of coke morphology by optical technique requires tedious work for the sample preparation [9], such as elaborate surface polishing procedure. The sequential analysis of optical images was also a time-consuming work. It was believed that at least seven images should be collected randomly from the well-polished coke sample in order to keep the analysis results reproducible and statistically valid [10]. Furthermore, thermally resultant coke sample might not have the enough amount and/or firm structure to support the traditional polishing process [11] in some cases, especially when the coking feedstock is rare and valuable (e.g. asphaltenes) [12], or even has a low coke yield (e.g. saturates) [13]. Our interest here is quantitative and rapid characterization of coke morphology, even in the severe aforesaid situations; therefore, methods based on generally quantitative morphology analysis and milligram quantities of reactant are required.

One of the most widely used methods to estimate the characterization of coke is the temperature-programmed oxidation (TPO). Because the technique could provide information regarding coke morphology [14], and thermal behavior of coke under oxidation conditions [15,16], it has been applied and well-accepted in the characterization of coke, such as quantifying the different carbon species from high-temperature treatment [17,18], estimating the kinetics of coke-O_2 reaction in a large variety of catalytic systems [19], and characterizing coke morphology [14,20].

Typical configurations in performing a temperature-programmed oxidation experiment include detection systems such

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as: Thermal Conductivity Detector (TCD) to measure CO_2 in a gas chromatography (GC) system [21], a calibrated infrared ray detector to measure CO_2 [14], thermo-gravimetric analysis (TGA) [22,23], and differential scanning calorimetry (DSC) [23–25]. Although the detection system in DSC could not provide as high sensitivity and resolution as the reported detection system [21], the signals would be still qualified for the distinguishing and analyzing. Preliminary studies of coke [14,26] suggested that the thermal reactivity of coke under oxidation atmosphere was closely related to the structure of coke itself. Altin and Eser further illustrated [14] that the presence of large aromatic structures in the coke aligned in a pre-graphitic or graphic order (i.e. anisotropic carbon form) would reduce the oxidation reactivity compared with that of amorphous carbon (i.e. isotropic carbon form) and hydrogen-rich chemisorbed carbon species. The planarity of constituent lamellar molecules even in the graphitizing carbons varied as the size of the optical texture of the anisotropic coke changed [27]. It was, therefore, believed that [1] the reactivity of carbons within the ordered molecules in the anisotropic structures under oxidation would increase as the lamellar molecule became more defective, which might be caused by heteroatoms and steric effect. Considering the structural aspect of thermal coke, a relationship was implied between anisotropic contents of coke and the reactivity of coke towards oxidizing gas [1]. A quantitative and rapid characterization of coke morphology is thus demonstrated in this study by analyzing the burnoff profiles resulted from TPO experiment thoroughly, and sequential correlating it with coke morphology obtained from optical observation.

2. Materials and methods

2.1. Thermal coke samples preparation

The coke samples were prepared from four vacuum residues (defined as VRA, VRB, VRC, and VRD) and the fractions (i.e. saturates, aromatics, resins, and asphaltenes) separated [28] from VRD in an autoclave under inert atmosphere. The testing pressure was preset to 0.5 MPa in order to acquire enough firm coke deposit. The autoclave was immersed in a reaction bath of 500 °C for 2 h. When carbonization was finished, the resultant coke column was taken out and cut longitudinally into two halves, and one half was then introduced into mold with the cutting surface upward. In the case of saturates carbonization, the coke deposit was quite rare. Standard high-purity Al_2O_3 was thus used as the carrier for the microcarbon particles.

2.2. Polarized light optical microscopy

The sequential polishing pretreatment of Siskin et al. [2] was followed in order to obtain representative samples for the polarized light optical observation. The image analysis method for quantitative estimating the optical anisotropic units was a point-counting procedure (800 point counts) [1]. The sizes of the anisotropic units in the texture, seen as isochromatic areas, were defined and described in a previous study [29].

An optical texture index (*OTI*) for each coke sample was thus calculated using the referenced formula, as described in detail in the research of Wang and Eser and Wang [30]:

$$OTI = \sum f_{\mathrm{i}} \times (OTI)_{\mathrm{i}} \tag{1}$$

where f_{i} is the numerical fraction of anisotropic isochromatic unit in textures, and (OTI_{i}) is the factor assigned to each kind of anisotropic unit [29]. Usually, thermal coke is comprised of small mosaic anisotropic carbon forms (optical texture sizes ranging from less than 1 μm to 10 μm), and relatively large domain anisotropic carbon forms (more than 10 μm). A standard scale mark of 10 μm was thus engraved in the image for an easier understanding of the morphology of coke sample.

2.3. Analysis of cokes with TPO technique

The coke samples used in optical experiments were taken out from the molds, and prepared for the TPO analysis (Linseis STA PT1600, Germany). Labeled Coke samples were then all ground to powder of 120–130 mesh in order to minimize diffusion effects in the tests [19] and keep the coke particle distribution in a rather narrow range. Coke samples with smaller size are also desirable on the condition that the size of sample is not lower than 60 μm (the upper size of anisotropic units in the texture); otherwise, the intrinsic morphology of coke would be undermined. 5 mg of sample was heated at a constant heating rate of 15 K min^{-1} within 50 mL min^{-1} of oxygen diluted in 50 mL min^{-1} of high-purity nitrogen from ambient temperature to 800 °C, at which complete oxidation of coke samples occurs [21]. Results from repeated experiments showed that the TPO thermal profiles were reproducible.

3. Results and discussion

3.1. Characterization of feedstocks

Four vacuum residues and SARA fractions originated from VRD were used as coking materials, selected properties of which are listed in Table 1. The data listed in Table 1 shows that the decreasing H/C atomic ratio of vacuum residue would lead to an evident increase of aromaticity, accompanied by the decrease of aliphaticity. It should be noted that the total amount of heteroatoms (S, N, and O) in VRD is the highest, which would mean that of all vacuum residues used, VRD contains the most active sites [31].

Table 1
Selected properties of selected coking materials.

Properties	Vacuum residues				VRD			
	VRA	VRB	VRC	VRD	Saturates	Aromatics	Resins	Asphaltenes
H/C	1.71	1.59	1.51	1.36	1.85	1.43	1.23	1.04
S, wt%	0.22	0.39	0.36	4.65	1.44	4.66	4.76	5.49
N, wt%	0.41	1.18	1.12	0.90	–	0.24	1.44	2.01
O, wt%	0.15	0.82	0.91	1.13	–	1.22	3.34	3.92
f_{A}[a]	0.13	0.20	0.27	0.38	0.08	0.36	0.42	0.53
f_{N}[b]	0.24	0.28	0.25	0.20	0.16	0.14	0.27	0.34
f_{P}[c]	0.63	0.52	0.48	0.42	0.76	0.50	0.31	0.13
MCR[d]	8.72	15.75	24.90	25.61	3.28	13.20	32.41	52.56

[a] Aromaticity (ratio of aromatic carbons to total carbons).

[b] Naphthenicity (ratio of naphthenic carbons to total carbons).

[c] Aliphaticity (ratio of paraffinic carbons to total carbons).

[d] Micocarbon residue determined according to ASTM D4530-11 [33].