Combustion and Flame 163 (2016) 447–460

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Reaction pathway of coal oxidation at low temperatures: a model of cyclic chain reactions and kinetic characteristics

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ARTICLE INFO

Article history:
Received 10 June 2015
Revised 14 October 2015
Accepted 15 October 2015
Available online 17 November 2015

Keywords:
Coal oxidation
Active sites
Quantum chemistry calculation
Activation energy
Chain reaction

ABSTRACT

Organic chemical reactions cause the temperature rising during coal oxidation; however, because of the complex structure of coal, it is difficult to analyze and characterize the reactions involved in coal low-temperature oxidation. To date, a main reaction pathway describing the heating progress during coal oxidation has not been proposed. Here, a series of cyclic chain reactions is presented to describe the oxidation mechanism during coal spontaneous combustion using quantum chemistry calculations. Main active sites and their molecular models were built. Three interactive modes of active orbitals and detailed reaction sequences of coal oxidation are proposed. The structural parameters and thermodynamic data were calculated and the orders of reactions for transformations between functional groups were identified based on their activation energies. The reaction pathway was constructed based on functional transformation relationships and the order of reactions. The results show that main reactions occurring during coal oxidation can be defined as the reactions of oxygen and hydroxide free radicals reacting with coal active sites. Methyne and carbon free radicals reacting with oxygen is the initial reaction during coal oxidation. The decomposition of peroxides linking the reaction pathway form cyclic chain. Hydroxyl and aliphatic hydrocarbon radicals as key of chain reactions consumes coal active sites and oxygen continuously. Aliphatic hydrocarbons appear to contribute more to heat release during coal oxidation due to greater heat release and lower activation energy of their reactions. Limited spontaneous reactions maintain constant apparent activation energy for the oxidation until the chain reactions are generated; the apparent activation energy then increases. Low-ranking coals have higher apparent activation energies during oxidation due to more oxygen-containing groups and side chains contain more reactions with higher activation energy. Results from this study can improve understanding of mechanism of coal oxidation and provide a guide to forecasting and preventing spontaneous combustion of coal in underground coal mines or coal stockpiles.

1. Introduction

The spontaneous combustion of coal at low temperatures is very complicated. Owing to the complex structure of coal, combustion generally results from multiple sequences of reactions occurring in the oxidation process. Because of the huge industrial losses and the need to prevent spontaneous combustion, studies of coal oxidation are still urgently needed by mining engineers and mine operators. Knowledge of coal oxidation characteristics at room temperature not only assists in understanding the coal's self-heating during storage or transportation, but also help control the spread of coal fires and the greenhouse gases generated from such oxidation.

It is well known that chemical interactions between coal and oxygen at low temperature can cause the spontaneous combustion of coal. Most such reactions occur on active sites [1–7]. The reaction steps that initiate the oxidation have been investigated by several researchers [8–12]. Wang et al. [7] summarized the reaction steps and built a schematic diagram of the chemical mechanism for the chemisorption sequence. Reaction mechanisms for the spontaneous low-temperature combustion of coal are controversial (such as those involving the formation and decomposition of hydrogen peroxide [12,13]), and most reaction schemes are inferred from the dissociation energies of relevant bonds in the coal macromolecular structure. It is therefore necessary to further examine the mechanism of reactions and reaction energy barriers in coal oxidation.

Quantum chemical calculations are an effective method of analyzing reaction mechanisms [14–17]. As quantum theory is developing, calculations of the energy and heat generated during reactions are becoming more accurate, especially for small chemical structures. Because coal is a large-scale molecular structure, it is difficult to calculate its oxidation reactions directly. However, previous research findings [17] show that aromatic structures in coal are stable and the chemical characteristics of active groups are unaffected by these

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http://dx.doi.org/10.1016/j.combustflame.2015.10.019
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Table 1
Proximate analyses, heating, hydrogen and H/C of coal samples 0.04–0.075 mm in size.

Species	Proximate analyzes (%)				Heating (kJ/g)	Hydrogen (%)	H/C	*Ro* (%)	Coal rank
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{net, ad}$	H_{ad}			
BZ	9.86	20.65	30.01	34.08	21.81	4.49	0.79	0.37	Lignite B
YM	12.15	6.82	33.67	47.36	29	4.79	0.61	0.47	Subbituminous
DFS	6.19	6.83	26.04	60.94	31.13	4.78	0.58	0.53	Bituminous D
HB	1.11	22.14	21.4	55.35	26.39	4.14	0.42	1.23	Bituminous B
XQ	0.95	14.47	12.04	72.54	29.679	3.64	0.30	2.16	Anthracite C

M_{ad}, moisture; A_{ad}, ash; V_{ad}, volatile matter; FC_{ad}, fixed carbon; $Q_{net, v, ad}$, net calorific value at constant volume and air dry basis; H_{ad}, hydrogen content on a dry basis; Ro, vitrinite reflectance index.

rings. Hence, single ring linking active sites as active fragments in coal structure are used to study the mechanisms of coal oxidation using quantum chemical methods. Shi et al. [17] proposed eight reactions that confirm that H_2O can be produced directly from the hydroxyl free radicals (HO•) and hydroxyl groups (R–OH). The activation energy to produce CO_2 is 80 kJ/mol. Florez et al. [18] applied a 9,10-dihydroanthracene model to study a peroxide intermediate which leads to a quinone reaction product in coal. Although various molecular models have been built to study the mechanism of reactions of active sites in coal oxidation, more models are demanded in order to get more reasonable result. In addition, related computations and simulations based on the above models only focus on the mechanism of a single reaction step: order and relationship of reactions of coal active sites are not usually discussed. Moreover, the relationships between all reactions cannot be described by a single or partial activation energy, and changes of enthalpy. Cyclic chain reaction pathway for coal oxidation therefore still needs to be developed.

Such a reaction pathway can be established based on analyses of detailed reaction sequences. It should be noted that the number of the sequences here increases with temperature rising as more reactions are activated. Accordingly, it is needed to explore main active sites participating in reactions activated by rising temperature, instead of only limited specific sites at a certain temperature. In this work, the main active sites and their typical molecular models in coal oxidation are built. The activation energies and enthalpies of reactions for these active sites are then calculated using quantum chemical methods. The order of reactions can be identified in accordance with the order of activation energies to describe the relationships between the active sites. Based on these, the main reaction pathway is built and forms a cyclic chain reaction which is a sequence of reactions where a reactive product or by-product causes additional reactions to take place. The segmented feature of the cyclic chain reaction is good agreement with the main features obtained from calorimetric experiments with coal.

2. Experimental and methodology

2.1. Samples preparation

Five typical Chinese coal samples, lignite (BZ from Beizao mine in Shandong), jet coal (YM from Yima mine in Henan), non-coking coal (DFS from DaFoshi mine in Shanxi), coking coal (HB from Yangliu mine in Anhui), and anthracite (XQ from Xinqiao mine in Henan) coal, were tested. The coal samples were ground to the size range from 0.04 mm to 0.075 mm and then dried for 24 h at a temperature of 313 K. The proximate analyses are shown in Table 1.

2.2. Infrared spectroscopy

The characteristics of the functional groups on the coal surfaces were collected by Nicolet 6700 Fourier Transform infrared spectrometer in the wave number range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}. Pure ground KBr was used for the reference spectrum. Each dry coal sample (4 mg) was ground to a particle size of 0.038 mm–0.075 mm under an inert atmosphere in a glove box and then analyzed using the diffuse reflectance accessory. Each spectrum is the average of 64 scans.

2.3. Calorimetric experiments and activation energy analysis

A C80 microcalorimeter manufactured by Setaram was used for the calorimetric measurements. The experimental procedure has been described in detail by Vieira et al. [19]. The heat generated during the oxidation of three coal samples (XQ, HB, DFS), shown in Table 1, was measured.

The coal samples were ground to a particle size ranging from 0.18 mm to 0.25 mm under an inert atmosphere in a glove box. The carrier gas for the calorimeter was dry air with an oxygen concentration of 20.96%, which was passed through the cell at a rate of 100 ml/min. About 1600 mg of coal sample was put into the calorimeter cell. The sample was then heated from 30 °C to 200 °C at 0.05 °C/min. Similar experiments were carried out at heating rates of 0.08 and 0.1 °C/min.

From the calorimetric experiments, the heat released by the coal was derived. According to the isoconversional differential method, the activation energies of coal samples at different temperatures can be obtained from experimental data at different heating rates using the *AKTS-Thermokinetics* software. From the experimental results, the heat flow at each temperature can be obtained. The heat release is therefore the integral of heat flow over a temperature range, and the change of heat release with increasing temperature can be obtained as shown in Eq. (1). In the *AKTS-Thermokinetics* software, the process (a) and the reaction rate (da/dt) are calculated based on Eqs. (2) and (3):

$$Q = f(T) = g\left(\frac{1000}{T}\right) \tag{1}$$

$$\alpha_T = \frac{Q_T}{Q_s} = \frac{1}{Q_s} g\left(\frac{1000}{T}\right) \tag{2}$$

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = \frac{\beta}{Q_s} g'\left(\frac{1000}{T}\right) \tag{3}$$

where Q *is* the heat release of the coal sample for a specific heating rate, T is the temperature of the sample (°C), and β is the heating rate (°C/min), α: reaction progress, Q_T is the heat release before T temperature, Q_s: is the total heat release in experiments, α_T: reaction progress at temperature T, $f(\alpha)$: model function, g' is the differential coefficient of model function g.

According to Eq. (3), three curves of da/dt as a function of $1000/T$ can be obtained for the three heating rates ($\beta = 0.05$, 0.08, and 0.1). According to the c (Eq. 4) [20], ln $(A(a)f(a))$ and E are constant for one process at different heating rates. Hence, the Friedman [21] analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate da/dt as a function of the reciprocal temperature at different degrees of conversion, a. The function of the isoconversional differential method is shown in Eq. (5).