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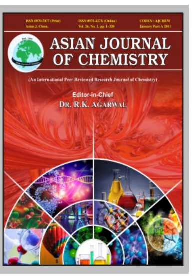

Kinetic Study of the Changes in Element Occurrence During Low-Temperature Oxidation of Coal

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Complex macromolecular matrix of coal is divided into the elements of C, O, H, S and N, which are all involved into the concerned reaction. Based on the changes in element occurrence during coal oxidation at low temperature, the pseudo-first-order reaction kinetics was used to evaluate the kinetic characteristics of coal oxidation. Coats and Refern's as well as Horowiz and Metzger's models were also used to model the changes in element occurrence. The activation energies obtained by the pseudo-first order kinetic have been found to be almost similar to those calculated by applying the Coats and Redfern's equation and the energies are higher when Horowitz and Metzger's equation is applied. The release of element H shows the highest rate constants (K) and lowest activation energy value (E_a) when compared with these values for C and N. A kinetic compensation effect between K and E_a was observed for the changes in element occurrence.

Keywords: Coal, Low-temperature oxidation, Element occurrence, Kinetics.

INTRODUCTION

Low-temperature oxidation of coal has been extensively studied by a number of investigators because the reaction between coal and oxygen can lead to the deterioration of the technologically useful properties and the emission of greenhouse-relevant gases and the release of toxic gases threatening the health of local inhabitants[1]. Furthermore, this reaction may also lead to self-heating and subsequent spontaneous combustion in coal mines and stockpiles[2,3].

The molecular structure and composition of coal is extremely complex and irregular, which causes the disturbance in experimental test of coal spontaneous combustion. Consequently on the practical side, progress in the science of self-heating leading to useful preventive methodologies with wide and extensive applicability on industrial level is yet to be fully developed[4]. Tang *et al.*[5-7] applies a series of small-molecule model compounds to simulate the coal macromolecular structure oxidation. In fact, aerial oxidation of coal principally involves the changes in C, H, O, S and N occurrence in coal matrix, which plays an important role in this oxidation process.

This process involves the incorporation of oxygen into the coal matrix and the release of other elements from the coal matrix. However, less work on the changes in element occurrence during low-temperature oxidation of coal has been reported in the literature. In previous work, the kinetic and thermodynamic characteristics of low-temperature oxidation of coal have been presented[8]. It is anticipated that the change in each element occurrence in coal matrix is different, meaning that the reaction activities of these elements in coal matrix vary from each other and each element plays different roles during the process of spontaneous combustion of coal. However, which dynamic kinetic equation followed by the changes in element occurrence is not clear currently.

In this paper, the complex macromolecular matrix of coal was divided into elements C, O, H, S and N, which are involved in the oxidation reaction. Based on the changes in element occurrence during coal oxidation at low temperature, the pseudo-first-order reaction kinetics was used to evaluate the kinetic characteristics of coal oxidation at low temperature. Furthermore, Coats and Redfern model as well as Horowiz and Metzger model were also used to changes in element occurrence during low-temperature oxidation of coal in order to find out which of the dynamic models is the best in explaining this process. The active energies and frequency factors were also been calculated to investigate the role of each element playing during the process of coal self-heating.

EXPERIMENTAL

A high volatile bituminous coal obtained from the Chinese Shendong coal mine, was used in this study. The coal sample was crushed and sieved to obtain particle sizes in the range of 0.125-0.180 mm and then stored in an airtight container prior to experiments. It should be noted that, the Shendong coal had high pyritic sulfur content, making up 80 % (wt. %) of the total amount of sulfur.

The experiments of coal oxidation were carried out in petri dishes, which were placed in a specially designed temperature-controlled air convection oven. On each petri dish, about 3 g of the coal sample was uniformly distributed in a layer having an average thickness of less than 2 mm. For each experiment, seven petri dishes were uniformly placed in the oven. Coal samples were non-isothermally oxidized to a maximum temperature of 200 °C with a slow heating rate of 1 K min^{-1} in air under normal atmospheric pressure. During each experiment, one of the seven petri dishes was withdrawn at each of the following temperatures: 50, 75, 100, 125, 150, 175 and 200 °C. Each coal sample was then cooled to room temperature in a desiccator with silica gel to minimize humidity and avoid further oxidation. Finally, the samples were kept in airtight polypropylene bottles. The experiment was then repeated six times in order to minimize experimental errors and obtain enough oxidized coal samples for the proximate and ultimate analyses. Throughout the study, the proximate and ultimate analyses were performed at fixed time points. In addition, these analyses were repeated twice in order to minimize experimental errors.

RESULTS AND DISCUSSION

Evaluation of the kinetic characteristics of the changes in element occurrence during coal oxidation at low temperature was performed using the pseudo-first-order kinetics. For comparison purposes, other two dynamic models, including Coats and Redfern's model[9] and Horowitz and Metzger's model[10] were also introduced in this study.

Plots of ln k against 1/T for these five elements show straight lines as represented in Fig. 1. This suggests that the changes in these five elements occurrence of during slow low-temperature oxidation coal in air follow the pseudo-first order kinetics. Table-1 shows the kinetic parameters, namely, specific rate constants (K), activation energy values (E_a) and frequency factors (A) for the changes in element occurrence. It can be seen that the activation energies for the changes in element occurrence showed different trends. The activation energy values for C, H and N were calculated and found to be 31.70, 4.66 and 37.47 kJ mol^{-1}, respectively. The highest activation energy was found for the changes in N occurrence because this element exists in a relatively stable form and a significant amount of energy is required to release nitrogen species. Lower activation energy found for the release of H than the release of C suggests that the H-containing group is more easily attacked by molecular oxygen to form hydroperoxide intermediates.

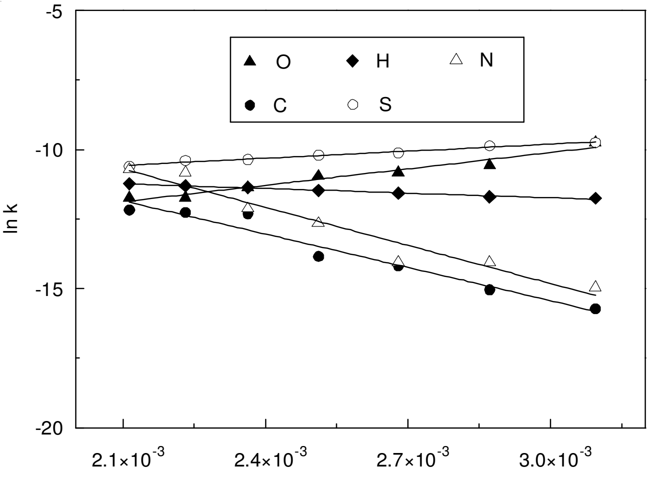

Fig. 1. Plots of ln k against 1/T for the changes in element occurrence

It is interesting that the negative activation energies have been observed for the changes in O and S occurrence. A typical example is that a negative activation energy was observed in the process of the adsorption and cracking of *n*-alkanes over ZSM-5[11], which is similar to the changes in O occurrence during low-temperature oxidation of coal. This phenomenon is a consequence of the competition between two effects *i.e.*, the increase of intrinsic kinetics with temperature and the decrease of adsorption strength and the concentration of active intermediates with temperature. The negative activation energy values for the changes in S occurrence may be related to the exothermic process when elements of S are transformed.

In view of the results obtained from the pseudo-first order kinetics, a comparison has been made using the two model equations. In order to test the first model equation, the value

TABLE-1
KINETIC PARAMETERS FOR THE CHANGES IN ELEMENT OCCURRENCE DURING OXIDATION OF COAL

Temperature (T, K)	Activation energy (E_a, KJ mol^{-1})					Frequency factor (lnA, s^{-1})				
	C	H	O	S	N	C	H	O	S	N
323.15										
348.15										
373.15	31.70^a	4.66^a	16.33^a	-7.01^a	37.47^a					
398.15	32.60^b	5.10^b	-18.25^b	-8.22^b	36.65^b	-4.02^a	-10.05^a	-16.00^a	-12.34^a	-1.22^a
423.15	41.75^c	17.32^c	-18.83^c	-10.87^c	50.17^c					
448.15										
473.15										

Note: a, calculated by the pseudo-first order kinetics; b, calculated by Coats and Redfern's equation; c, calculated by Horowitz and Metzger's equation of order (*n*) must be assumed first. Moreover, to test the second model equation, it is necessary to find out the values of T_s. According to Horowitz-Metzger's model[10], T_s can be determined by using the temperature at which $1-\alpha = 1/e = 0.3679$; the values $\theta = T-T_s$ are then calculated. The calculated T_s values are 442, 418, 365, 380 and 456 K for C, H, O, S and N, respectively. It can be seen that the size of T_s values for elements C, H and N are consistent with their activation energy values.

The linear fits for the two models were investigated and these data obtained have been plotted in Fig. 2 and 3, respectively. From Figs. 2 and 3, it can been observed that Coats and Redfern's model as well as Horowitz and Metzger's model show representative diagrams and in each case almost straight lines for the changes in element occurrence are observed. Since the changes in element occurrence during slow low-temperature oxidation coal follow the pseudo-first order kinetics, the activation energies have been calculated for n = 1. The activation energies and frequency factors evaluated from the slopes of the straight line and these results are also shown in Table-1. It can be seen that the values obtained from Coats and Redfern's treatment agree well with the values calculated by the pseudo-first order kinetics, whereas Horowitze Metzger method shows relatively higher values. For solid-state reactions, different models have been proposed depending upon the type of processes leading to the reaction. In the present case, the applications of Horowitz-Metzger and Coats-Redfern relations suggest a contracting cylinder kinetic model as an appropriate one for the mechanism of the changes in element occurrence[12]. However, the significant difference in activation energies data computed

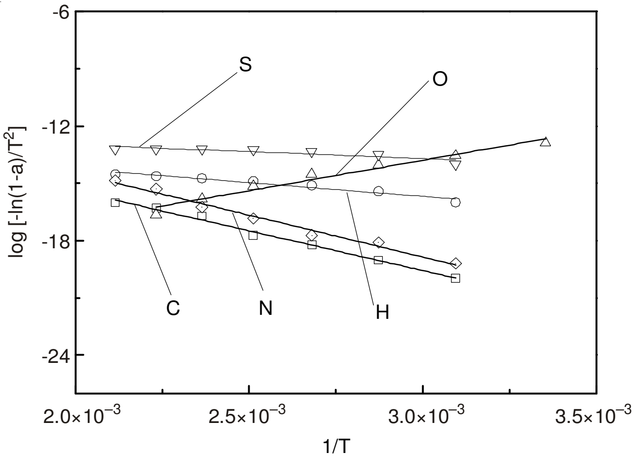

Fig. 2. Variation of $\log[-\ln(1-\alpha)]/T^2]$ against 1/T obtained from Coats and Redfern's model (n = 1) for the changes in element occurrence

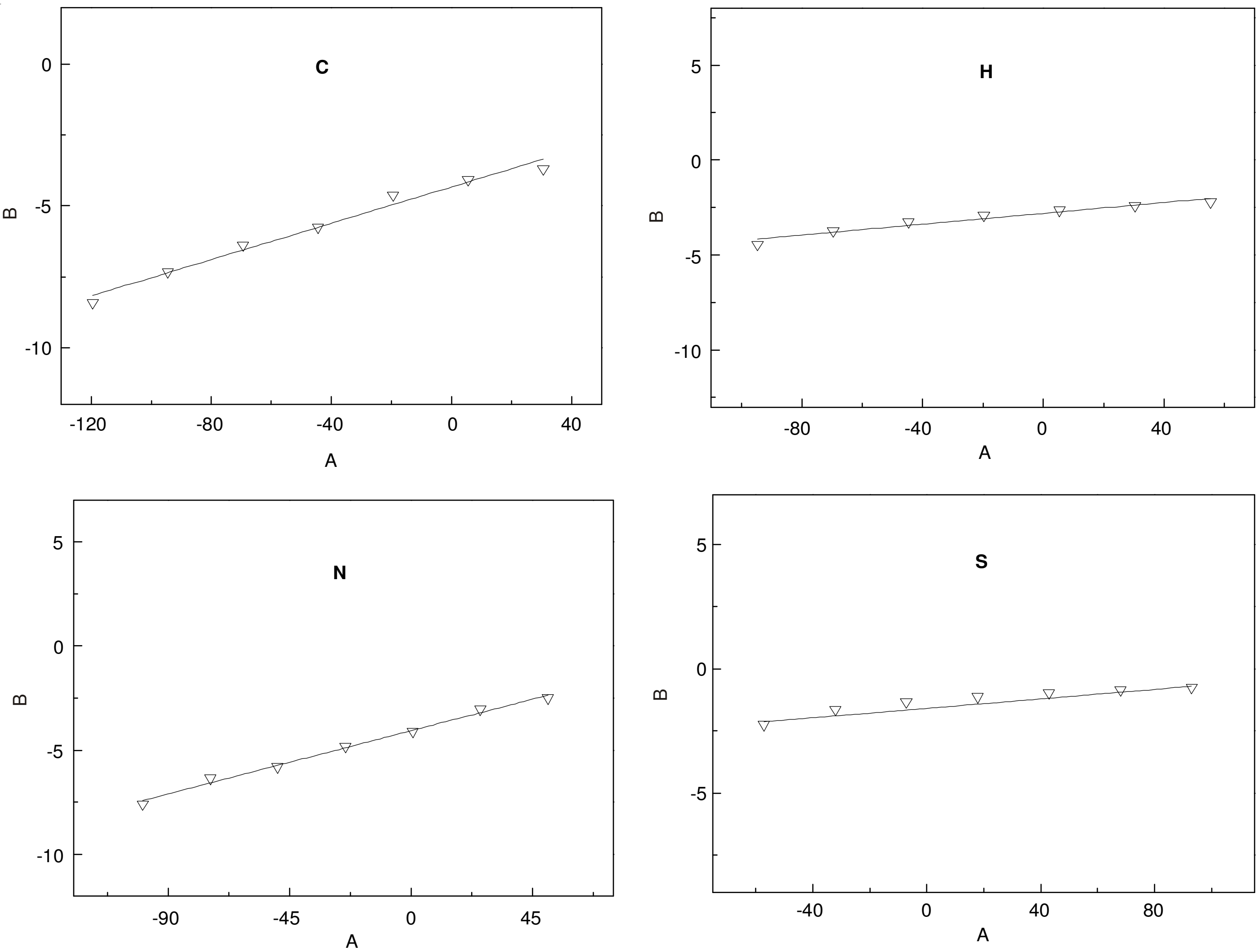

Fig. 3. Variation of $B = \log[-\ln(1-\alpha)]$ against $A = \theta$ obtained from Horowitz and Metzger's model (n=1) for the changes in element occurrence

by the Coats and Redfern's treatment and Horowitz and Metzger's treatment is unknown.

The frequency factors (A) calculated by the pseudo-first order kinetics has also been presented in Table-1. The common interpretation of the frequency factor is that it represents the number of successful collisions between the reacting species in the form of the activated complex[13]. The frequency factors computed by the pseudo-first order kinetics are very low, suggesting a very low rate of successful collisions for the formation of the activated complex. The low frequency factor values for the changes in element occurrence reflect the associated type of oxidation reaction because such types of reactions have low frequency factors. Because frequency factor values govern the formation of activated complexes, only a small number of activated complexes are likely formed, further slowing the oxidation reaction and affecting the rate constants.

Fig. 4 shows the relationship between ln A_{app} and E_{app} for the changes in element occurrence during low-temperature oxidation of coal. It can be seen that lnA indeed varied in linear proportion with E_{app}, exhibiting the so-called kinetic compensation effect, yielding the correlation $\ln A_{app} = m E_{app} + c$, where m is the slope and c is the intercept of the straight line. The kinetic compensation effect has been mentioned in kinetic studies of coal pyrolysis and gasification[14,15]. However, few studies have examined the kinetic compensation effect in the context of low-temperature oxidation of coal. The kinetic compensation effect suggests a similar increase in the population of apparent active sites with respect to the increase in the apparent energy barrier for the evolution of different elements during low-temperature coal oxidation.

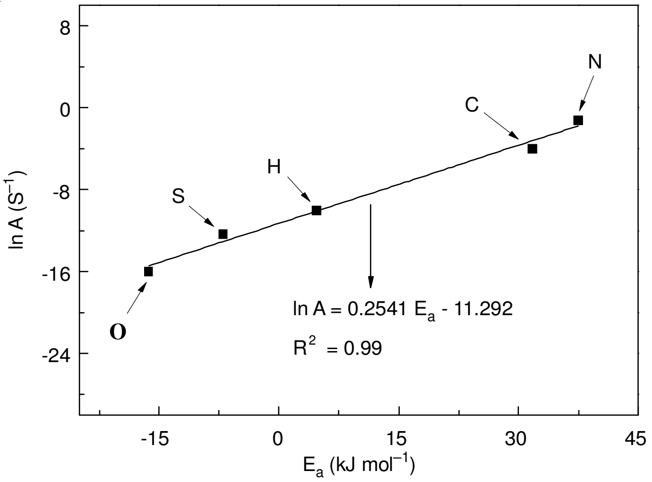

Fig. 4. ln A_{app} *versus* E_{app} for the changes in element occurrence

On the basis of the results above, the kinetic characteristics for the changes in element occurrence reflect the nature of coal self-heating during low-temperature oxidation of coal. The mechanism of coal oxidation at low temperature can be interpreted in terms of self-oxidation, which is a chain reaction. The comparatively lower activation energy associated with the release of H than C and N suggests that H-containing groups can be more easily attacked by molecular O_2 to form hydroxide intermediates. The low-temperature oxidation of coal can be initiated by the attack of molecular oxygen on the hydrogen in the a position. Then, the oxygen attacks carbon and other elements, which requires more energy. The heat produced during the changes in O and S occurrence provides energy for further coal oxidation. The low rate constant and frequency factor values found in all cases represent the considerably low levels of oxidation that occurred and reflect that the reaction was kinetically very slow.

Conclusion

The process of coal oxidation at low temperature involves the changes in element occurrence in coal matrix, which plays significant in the hazard of coal self-heating. The changes in element occurrence during slow low-temperature oxidation coal in air follows the pseudo-first order kinetics. It has also been observed that the values obtained from Coats and Redfern's treatment agree well with the values calculated by the pseudo-first order kinetics, whereas Horowitze Metzger method shows relatively higher values. The low rate constant and frequency factor values found in all cases represent the considerably low levels of oxidation that occurred and reflect that the reaction was kinetically very slow.

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