CHARACTERISTICS OF OXYGEN CHEMISORPTION ON POROUS COAL CHAR

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Abstract–Oxygen chemisorption on a porous coal char was investigated by a typical consecutive pyrolysis and chemisorption experiments in a thermogravimetic analyzer. Small amounts of carbon-oxygen surface complexes are gasified to CO and CO_2 during the oxygen chemisorption at 423 K. The kinetic equation of oxygen chemisorption on porous char including gasification of surface oxides well represents the chemisorption/gasification behavior of oxygen on the coal char. The activation energy and the frequency factor for oxygen chemisorption on coal-char are found to be 57 kJ/mol and 9.16×10^6/hr, respectively.

INTRODUCTION

The reaction of oxygen with solid carbon has been extensively studied for several decades [Fung and Kim, 1990; Laine et al., 1963; Park et al., 1991; Su and Permutter, 1985; Walker et al., 1991; Zhang et al., 1994]. It is generally accepted that the reaction of oxygen with carbon forms surface complexes through dissociative adsorption of oxygen on the carbon-free sites so that the surface oxides subsequently are gasified to CO and/or CO_2. As a result of gasification of surface oxides (removal of carbon atoms) new free sites are exposed for subsequent chemisorption of oxygen. Thus, chemisorption/gasification rate is a factor affecting the amounts of surface oxygen complexes. Laine et al. [1963] reported that the reaction rate constant of the carbon-oxygen reaction should be expressed based on the active surface area (ASA) rather than the total surface area (TSA) of the reacting carbon. The importance of ASA, also, has been conformed by many investigators [Radovic, 1991]. In general, ASA of carbon is determined by chemisorption of oxygen at low temperature. The chemisorption conditions are selected to satisfy the sufficiently high temperature to achieve equilibrium in a reasonable period of time and sufficiently low temperature to eliminate concurrent carbon gasification. Because small amounts of surface oxygen complexes are gasified during the chemisorption, the measured ASA of porous carbon is smaller than true ASA. Recently, Walker et al. [1991] reported that the gasification rate of carbon based on ASA cannot represent the true reaction rate since the carbon-oxygen surface complex consists of the stable complex and the fleeting oxygen complex. There are numerous studies on the kinetics of oxygen chemisorption on carbon, but the proposed models in the literature [Bansal et al., 1970; Cheng and Harriott, 1991; Waters et al., 1986; Floess at al., 1991; Lee et al., 1995] cannot fully represent the experimental data of the high coverage.

In this study, characteristics of oxygen chemisorption/gasification on a microporous coal char have been investigated at lower temperature. Oxygen chemisorption was determined by measuring the weight gain, and the gasification of surface oxygen complexes was observed by analysis of the product gas. A modified kinetic equation of oxygen chemisorption on the porous coal char, including the effect of gasification of surface oxides, is proposed. The results obtained from the TGA experiment are compared with the kinetic equations of the present and previous [Cheng and Harriott, 1991] studies.

MODIFICATION OF KINETIC EQUATION

Applying the collision theory to the activated and dissociative chemisorption, the following rate equation can be obtained [Hayward and Trapnell, 1964].

$$\gamma_a = \frac{1}{2}\frac{dn_a}{dt} = \sigma\frac{P}{\sqrt{2\pi m k_b T}}\left(1 - \frac{n_a}{n_s}\right)^2 \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where γ_a is the chemisorption rate in molecules/m²s, $P/\sqrt{2\pi m k_b T}$ is the total particle flux based on the kinetic theory, n_a is the number of active sites covered by adsorbate at time (sites/m²), n_s is the total number of active chemisorption sites (sites/m²), E is the activation energy of chemisorption, and σ is the probability factor.

Because the number of active sites covered by adsorbate on the carbon depends on the mass of chemisorbed oxygen on the carbon free sites, Eq. (1) may be written as

$$\gamma_a = \frac{dW_a}{dt} = \sigma\frac{P}{k_w\sqrt{2\pi m k_b T}}\left(1 - \frac{W_a}{W_s}\right)^2 \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

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where W_a is the weight of chemisorbed oxygen at time t, W_s is the maximum weight of the oxygen chemisorbed, k_w is the weight of an oxygen molecule. Small amounts of surface oxygen complexes are gasified to CO and CO_2 during the chemisorption at lower temperatures. In fact, the weight gain recorded by TGA could be the result of chemisorption and gasification reactions taking place at the carbon surface. So, W_a and W_s could not be measured exactly in TGA. Therefore, the following kinetic equation is proposed as

$$\gamma_a = \sigma \frac{P}{k_w \sqrt{2\pi m k_b T}} \left(1 - \frac{W_a}{W_s}\right)^2 \exp\left(-\frac{E}{RT}\right) f(W_a) \qquad (3)$$

where $f(W_a)$ is the rate correction factor considering the gasification of the labile carbon surface oxides at time t. It is assumed that the labile carbon is formed by pyrolysis of coal, that it is immediately gasified in the presence of oxygen. Therefore the labile carbon is decreased with the reaction time, so the rate correction factor, $f(W_a)$, is assumed to be W_c/W_a. Integrating Eq. (3) yields

$$\frac{\theta}{(1-\theta)} + \ln(1-\theta) = k \exp\left(-\frac{E}{RT}\right) t \qquad (4)$$

where $\theta = W_a/W_s$ and k is $\sigma P W_c / W_s k_w \sqrt{2\pi m k_b T}$.

And when the gasification is ignored in the chemisorption kinetic equation, Eq. (4) becomes

$$\frac{\theta}{(1-\theta)} = k_o \exp\left(-\frac{E}{RT}\right) t \qquad (5)$$

where k_o is $2\sigma P / \sqrt{2\pi m k_b T}$.

EXPERIMENTAL

The coal-char used in this study was prepared from Datong coal (China), and the proximate, ultimate and ash analyses of the coal (-40 mesh fraction) are given in Table 1. The coal was devolatilized under a flow of pure N_2 (>99.999 %) and oxygen was adsorbed on the char in the stream of air in a TGA apparatus (Cahn, TG121 system). As a carrier gas, purified N_2 was used and impurities in N_2 were eliminated by Oxysorb and silicagel.

A typical scheme of the consecutive pyrolysis and chemisorption experiments is shown in Fig. 1. About 10 mg of coal was placed in a platinum pan that was enclosed by a quartz tube of the Cahn weighting unit. The coal samples were purged with N_2 for 30 min, and heated to 1,073 K at a heating rate of 30 K/min. To decompose and evaporate the volatile matter, the treated samples were kept at 1,073 K for 15 min. Thereafter, the samples were cooled to a predetermined reaction temperature and held a few minutes to permit temperature equilibration before air flow (50 ml/min) was introduced. After the chemisorption reaction, the samples were reheated to 1,073 K at a heating rate of 30 K/min to obtain ash.

The micro-reactor system consists of a quartz tube (12 mm-i.d. ×250 mm-length) and a furnace. The coal samples (500 mg) were placed in a cell made of stainless steel sieve (250 mesh, 10×50 mm) surrounded by a quartz tube. The temper-

Table 1. Chemical properties of Datong coal

Proximate analysis (wt%)	Moisture 3.92	Volatile matter 29.92	Fixed carbon 60.92		Ash 5.24
Ultimate analysis (wt%)	Hydrogen 4.01	Carbon 71.23	Nitrogen 0.94	Sulfur 0.78	Oxygen 23.04

Heating value (kcal/kg)	6420

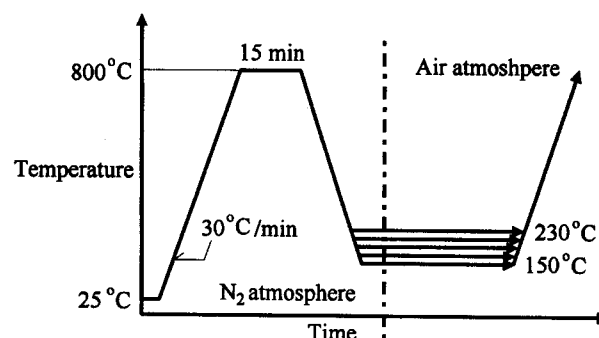| Ash analysis (wt%)	Al_2O_3 17.79	SiO_2 41.40	CaO 6.36	Fe_2O_3 28.21	K_2O 0.67	Na_2O 0.24	MgO 2.90	SO_2 1.62

Fig. 1. Typical scheme of consecutive pyrolysis and chemisorption experiments.

ature profiles in the micro-reactor were similar to that in the TGA (Fig. 1). Because of low concentrations of CO, CO_2 in the effluent gas, the flow rate of carrier gas was reduced from 1,000 to 50 ml/min after the pyrolysis of coal. Because the molecular weight of N_2 is nearly the same as that of CO, high purity He was used as a carrier gas instead of N_2. A mixture of He and O_2 gas was introduced through the cell during the chemisorption reaction. A mass spectrometer (VG Co., MMPC 200) was used to analyze the composition of gas samples.

RESULTS AND DISCUSSION

It is well known that surface oxygen complexes form on carbon as an intermediate during carbon gasification with oxidizing gases, and some complexes also form on carbon that is exposed at room temperature [Zhang et al., 1994]. Therefore, it is necessary to clean the carbon surface to remove the oxygen complexes before each chemisorption test. Thus pyrolysis of coal and chemisorption experiments were consecutively carried out in a TGA apparatus. Oxygen chemisorption is performed to determine the ASA of carbon. In general, it is accomplished at sufficiently low temperature to neglect gasification. In case of graphite, a temperature of 573 K usually satisfies this condition. Because coal char is more amorphous than graphite, oxygen chemisorption of Datong chars should be carried out at a temperature lower than 573 K.

The chemisorption of oxygen on the coal-char at different temperatures is shown in Fig. 2, in which the curves show the usual adsorption characteristics, namely, a rapid initial rate that quickly decelerates. The amounts of oxygen chemisorption at 423, 463 and 483 K are almost the same after 40 hr,
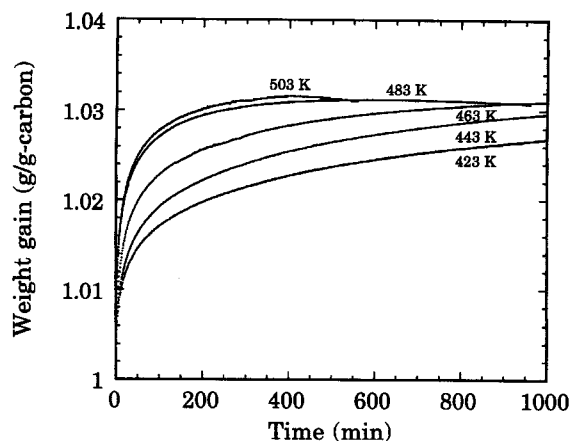
Fig. 2. Weight gain of the coal char during the oxygen chemisorption.

18 hr and 10 hr, respectively. At 423 K the weight of char increases continuously and the rate of increase becomes slower until 40 hours of oxygen exposure. Therefore, the active surface area of coal-char can be measured conventionally by oxygen chemisorption at 483 K. The active surface area of porous carbon can be calculated assuming that each chemisorbed oxygen atom occupies an area of 0.083 nm^2 [Laine et al., 1963]. The active surface area of Datong char pyrolyzed at 1,073 K is found to be 98 m^2/g.

It should be pointed out that a peculiar behavior is observed when the time of oxygen chemisorption is very long. The weight reaches a maximum in 7 hr after O_2 exposure at 503 K and 13 hr at 483 K, respectively. Also, when the carrier gas was switched from air to N_2 during the chemisorption, the weight of char slightly decreased (Fig. 3). From these data, it can be considered that the dangling carbons of coal-char are gasified during the chemisorption at 483 and 503 K. However, it is not clear whether gasification of surface oxides takes place at temperatures lower than 483 K. The product gas was analyzed to determine the possibility of gasification of surface oxides at other temperatures. Because of very low concentrations of CO, CO_2 in the effluent gas in the TGA experiment, a micro-reactor system was employed.
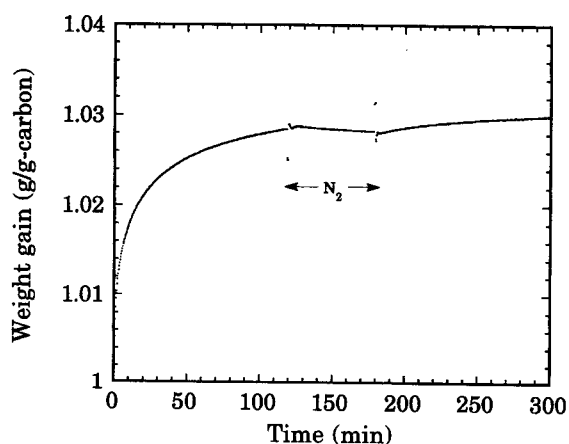

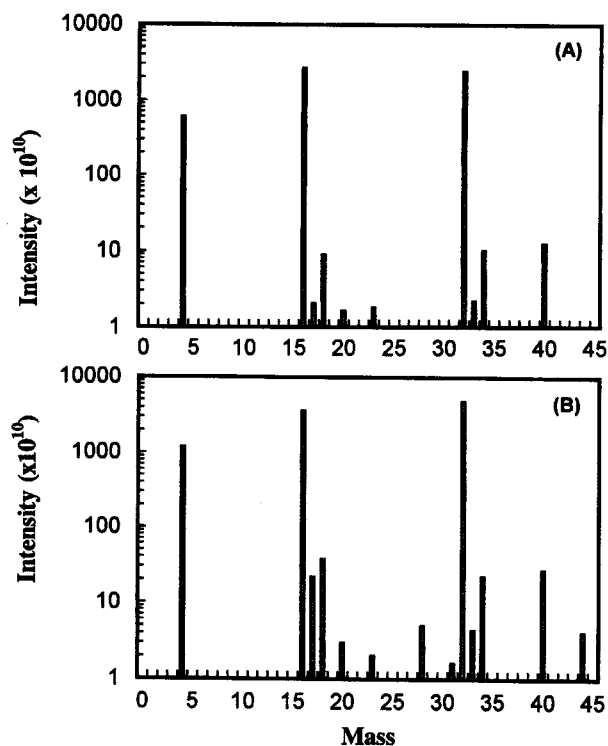**Fig. 3. Weight change of char by the exchange of the reaction gas during the chemisorption.**

Fig. 4. Typical histogram of the carrier gas.
(a) Just in front of the coal char bed, (b) After the coal char bed
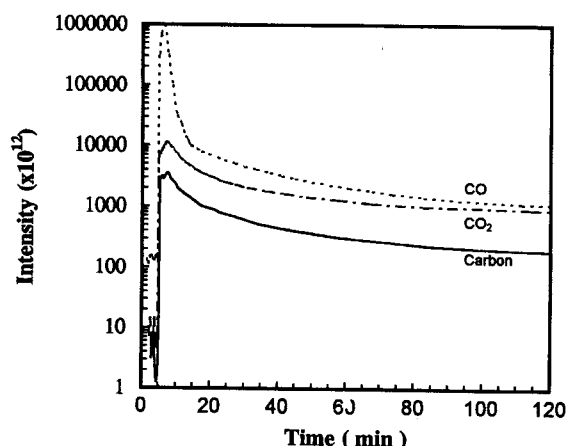

Fig. 5. Typical mass spectra of the effluent gas after the coal char bed.

A typical histogram of carrier gas in front of the coal char bed (a) and the effluent gas after the coal char bed (b) at 423 K is shown in Fig. 4. Also, a typical mass spectrum of the effluent gas after the coal char bed at 423 K is shown in Fig. 5. The characteristic peaks of CO (m/z = 28) and CO_2 (m/z = 44) from the effluent gas after the coal char bed clearly appear in the histogram and the mass spectra. This indicates that the carbon-oxygen surface complexes are gasified in the form of CO and CO_2 as reported in a previous study of Ismail et al. [1989] that oxygen chemisorption is accompanied by char gasification at temperature above 398 K.

The gasification is an irreversible reaction, although the gasification of surface oxides occurs simultaneously to a very small
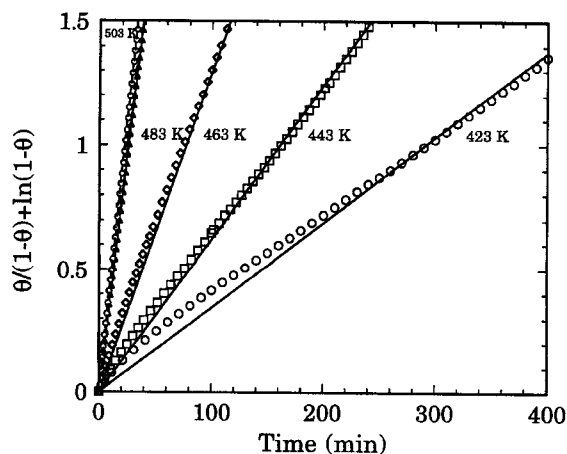
Fig. 6. Experimental data calculated from proposed chemisorption kinetic equation [Eq. (4)].
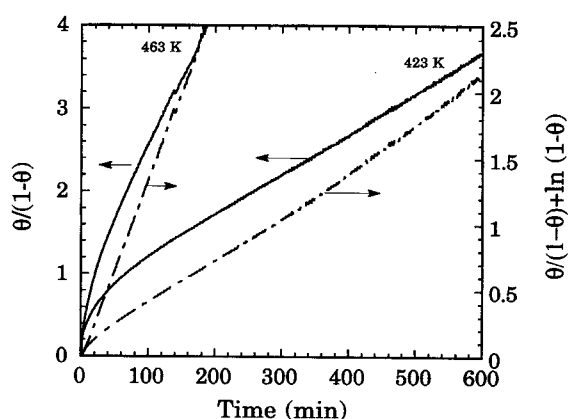

Fig. 7. Kinetic plots of oxygen chemisorption data solid line : with gasification [Eq. (4)], dashed line : without gasification [Eq. (5)].
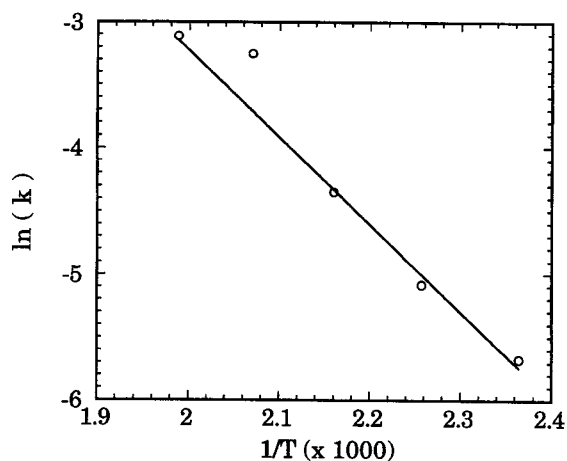

Fig. 8. Arrhenius plot of the oxygen chemisorption data with proposed kinetic equation.
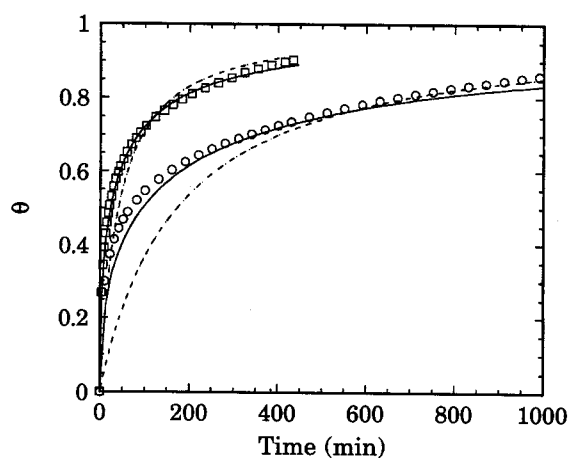

Fig. 9. Comparisons of the oxygen chemisorption on coal char. $\bigcirc$: 443 K, $\square$: 503 K, solid line [from Eq. (4)], dashed line [from Eq. (5)].

extent with O_2 chemisorption at the relatively low temperature. The weight gain recorded by TGA could be the result of chemisorption and gasification reactions taking place at the carbon surface. Therefore, the gasification of surface oxides term must be included in the kinetic equation of chemisorption of oxygen on porous carbon.

The chemisorption is calculated from the proposed kinetic equation of chemisorption on a porous carbon at 423 K, 443 K, 463 K, 483 K and 503 K that takes account of gasification of surface oxides [Eq. (4)], as shown in Fig. 6. The value of W_s in Eq. (4) is chosen at the maximum weight gain (daf basis) from the TGA data at different chemisorption temperatures. The results exhibit good linearity to the high coverage of oxygen at all the temperatures employed according to the proposed kinetic equation. The larger the value of W_s in Eq. (4), the better linearity to the high coverage is obtained.

For comparison of the kinetic equations, chemisorption data at 423 K and 463 K from Eq. (4) (with gasification) and Eq. (5) (without gasification) are replotted in Fig. 7. As can be seen, the data calculated from the proposed kinetic equation [Eq. (4)] exhibit linearity reasonably well to the high coverage, while the data calculated from Eq. (5) deviate appreciably at the low coverage.

The dependence of chemisorption rate on the temperature is shown in Fig. 8. The activation energy and frequency factor for O_2 chemisorption on Datong coal-char are found to be 57 kJ/mol and 2.38×10^6/hr, respectively. Ismail et al. [1989] reported that activation energy of oxygen chemisorption on Saran Char is 49.1 ± 3 kJ/mol, which is comparable to that of this study.

The amount of the chemisorbed oxygen calculated from the activation energy and frequency factor, and the experimental values are shown in Fig. 9. As can be seen, the proposed kinetic equation predicts well the experimental data to the high coverage, because the proposed chemisorption kinetic equation includes the gasification of surface oxide complexes on porous coal-char.

CONCLUSIONS

Based on the theoretical and experimental studies of O_2 chemisorption on porous carbon, the following conclusions can be drawn.

1. Small amounts of surface carbon-oxygen complexes are gasified to CO and CO_2 in the chemisorption reaction at 423 K.

2. Since gasification of surface oxygen complexes is the irreversible reaction, gasification should be considered in O_2 chemisorption kinetics of porous carbon.

3. For gasification, the kinetic equation of chemisorption of oxygen on porous carbon can be represented as

$$\frac{\theta}{(1-\theta)} + \ln(1-\theta) = k\exp\left(-\frac{E}{RT}\right)t$$

4. The activation energy and the frequency factor for O_2 chemisorption on coal-char are found to be 57 kJ/mol and 2.38×10^6/hr, respectively.

NOMENCLATURE

E : activation energy of chemisorption [J/mole]
k, k_o : frequency factor [-]
k_b : Boltzmann's constant [J/K]
k_w : weight of a oxygen molecule [kg]
m : molecular weight [kg]
n_a : number of active sites covered by adsorbate at time [sites/m^2]
n_s : total number of active sites [sites/m^2]
$f(W_a)$: rate correction factor $(= W_c/W_a)$ [-]
P : pressure [Pa]
R : universal gas constant [J/mole K]
γ_a : chemisorption rate [molecules/m^2 s]
T : temperature [K]
t : time [sec]
W_a : weight of chemisorbed oxygen at time t [kg]
W_c : weight of labile carbon [kg]
W_s : maximum weight of the chemisorbed oxygen [kg]
σ : probability factor [-]

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