

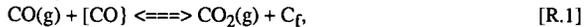
A Mathematical Model of Temperature Programmed Desorption of Oxygen Complexes From Porous Chars and Carbons

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Introduction

Temperature programmed desorption/mass spectrometry (TPD/MS) has become a popular technique for investigating the nature and behavior of oxygen surface complexes on carbons and chars (e.g., see [1-3]). Such studies have been generally useful in establishing certain qualitative aspects of the behavior of these surface complexes. We have been applying this technique in our laboratory as a probe of the energetic heterogeneity of coal char surfaces [4]. In Figure 1 are presented typical TPD spectra for CO and CO₂ obtained in our laboratory for a Pittsburgh #8 coal char sample gasified to 27.3% in oxygen. As can be seen, the spectra consist of two small, relatively broad CO₂ peaks, and a large CO peak with a high temperature shoulder. It is noted that these spectra are remarkably similar to those reported for other significantly different carbons (e.g., see [1-3]). We have interpreted the origins of these features in another publication [5]. Essentially, it appears that the first CO₂ peak at 600K is most probably due to intrinsic CO₂-liberating complexes, such as lactones and/or carboxylic anhydrides [2,3]; while the first CO peak is most probably due to intrinsic CO-liberating complexes, such as carbonyls and/or semi-quinones [2,3].

We have shown [6], however, that the second CO₂ peak, centered at about 900K, is at least partially due to CO₂ produced in the secondary reaction:



where [CO] is a surface complex with a single oxygen molecule, and C_f is a "free active site." The importance of this reaction was discovered in a series of experiments employing a number of coal chars over a large variation in heating rate. For those chars that exhibited significant porosity, it was noted that the total integrated amount of CO₂ exhibited a broad maximum at a heating rate ca. 100K/min, while the total oxygen balance (i.e., CO+2CO₂) remained invariant. The high temperature shoulder on the primary CO peak, evident in Figure 1, is hypothesized to be primarily due to re-adsorption of free CO(g) evolved during the course of the TPD [5]. This was determined from TPD experiments in which a previously "thermally cleaned" char surface was exposed to CO at low temperatures for a prolonged period of time. Subsequent TPD revealed a high temperature CO peak precisely at the location of the high temperature shoulder in Figure 1 [5]. This conclusion is also supported by the CO chemisorption results of Marchon et al. [7].

Recently, we have been directing our efforts at quantifying the information available from such desorption chromatograms. As one of the tools in this endeavor, we have developed a mathematical model. In the current paper, we present the essentials of this model and some sample results. We then compare some model predictions to experimental TPD observations. In this manner, we demonstrate the utility of the model and highlight areas where work remains to be done.

The Model

Even though there seems to be general qualitative agreement as to the basic features present in TPD spectra of surface oxides from carbonaceous solids, there is still very little actually known about the mechanisms involved in producing these features. Therefore, any model formulated at this time will almost certainly have to be modified to take into account new discoveries as we learn more about the processes that occur during TPD. Even so, we demonstrate here that even a rudimentary model is still a useful tool even at this stage of development to aid in the elucidation of the relevant mechanisms. It is in this spirit in which we present our work here.

One of the most elementary forms of the current model is based on the assumption of two distinct types of complexes on the carbon surface: (1) intrinsic CO₂-liberating complexes (e.g., lactones, carboxylic acids, carboxylic anhydrides); and (2) intrinsic CO-liberating complexes (e.g., semi-quinones and carbonyls). It is further assumed that the population of active sites at which these complexes are formed is distributed energetically, but that there is a finite number that is conserved during the course of the TPD experiment; i.e., the total concentration of active sites, C_t, is a constant. Based upon our previous work [5,6], we also allow for the secondary interactions [R.1], which interconvert the free oxides of carbons once they are produced within the char porosity.

In addition to the preceding, the model also allows for transport resistance. More specifically, in the version of the model presented here, we focus on a microporous char such that the primary resistance to transport lies in microporous regions; i.e., the larger pores present no transport resistance to the evolved gases. It is assumed, for the sake of simplicity, that the microporous regions are spherical with a characteristic radius, R. It is further assumed that the transport is activated. In any case, it is noted that this particular view is not necessary in order to predict the TPD spectra for non-transport limited conditions, and that different carbons and chars will obviously exhibit different transport characteristics. Consequently, it is expected that the model will have to be tailored appropriately in order to account for the actual conditions that obtain.

With the preceding assumptions in mind, the following dimensionless mass balances can be formulated for four species; i.e., two surface complexes and the two oxides of carbon, CO and CO₂:

$$\partial u_1 / \partial \tau = g_1 \nabla^2 u_1 + \phi_{d1} \theta_1 - \phi_1 u_1 \theta_1 + \phi_2 u_2 (1 - \theta_1 - \theta_2)$$

$$\partial u_2 / \partial \tau = g_2 \nabla^2 u_2 + \phi_{d2} \theta_2 + \phi_1 u_1 \theta_1 - \phi_2 u_2 (1 - \theta_1 - \theta_2)$$

$$d\theta_1 / d\tau = -\phi_{d1} \theta_1 - \phi_1 u_1 \theta_1 + \phi_2 u_2 (1 - \theta_1 - \theta_2)$$

$$d\theta_2 / d\tau = -\phi_{d2} \theta_2$$

where: $u_1 = \epsilon C_{CO} / C_t$ $\theta_1 = [CO] / C_t$ $\tau = t / t_d$
 $u_2 = \epsilon C_{CO_2} / C_t$ $\theta_2 = [OCO] / C_t$ $t_d = R^2 / D_{1,0}$
 $g_1 = \exp(-E_{1,d} / RT)$ $g_2 = (D_{2,0} / D_{1,0}) \exp(-E_{2,d} / RT)$ $r = r / R$

D_{1,0}, D_{2,0} pre-exponentials for the diffusivity for θ_1 and θ_2

C_t = mol active sites/cm³ microparticle

ϵ = void fraction of char microporous region

$\phi_{d1} = t_d k_{d1,0} \exp[-E_{d1} / RT]$, the desorption rate constant for θ_1

$\phi_{d2} = t_d k_{d2,0} \exp[-E_{d2} / RT]$, the desorption rate constant for θ_2

$\phi_1 = t_d k_{1,0} \exp[-E_1 / RT] C_t / \epsilon$, forward rate constant for reaction [R.1]

$\phi_2 = t_d k_{2,0} \exp[-E_2 / RT] C_t / \epsilon$, reverse rate constant for reaction [R.1]

The linear heating regimen provides the relationship between time and temperature: $\Theta = 1 + \Omega \tau$, where $\Omega = B t_d / T_0$, $\Theta = T / T_0$, B is the heating rate, and T₀ is the initial temperature. Surface heterogeneity is modeled using activation energies that are functions of surface coverage:

$$E_{d1} = E_{d1,0} - \alpha \theta_1; E_{d2} = E_{d2,0} - \beta \theta_2; E_1 = E_{1,0} - \gamma (\theta_1 + \theta_2); E_2 = E_{2,0} + \delta (\theta_1 + \theta_2)$$

The corresponding boundary conditions for a typical TPD experiment are:

$$u_1 = u_2 = 0 @ r = 1 \quad (\text{i.e., no external mass transfer resistance})$$

$$\partial u_1 / \partial \tau = \partial u_2 / \partial \tau = 0 @ r = 0 \quad (\text{symmetry condition})$$

The initial conditions are:

$$\theta_1 = \theta_{1,0}; \theta_2 = \theta_{2,0}; u_1 = u_2 = 0 @ \tau = 0$$

Since a TPD spectrum represents the *rate* of gas evolution vs temperature (or time), the dimensional

evolution rate from the char is determined by the flux at the exterior of the microporous regions, J:

$$\text{Rate} = (A_p/V_p) J = - (3 C_1/\epsilon t_d) (\partial u_1/\partial r)_{r=1}; \text{ mol/cm}^3 \text{ s,}$$

where A_p, V_p are the exterior surface area and the volume of the microporous regions, respectively (for spherical geometry, $A_p/V_p = 3/R$). The resultant model was solved using the code PDECOL [8].

Results and Discussion

In Figure 2 are presented results of the model for three heating rates under conditions where there is a single activation energy for the desorption of each of the surface species. As can be observed, the peak maximum is quite sensitive to heating rate, moving to higher temperatures with heating rate, as expected for first order desorption processes. In order to match the peak temperatures of 600K and 1000K evident in the data in Figure 1 at 100K/min, the required activation energies are 38.8 and 66.7 kcal/mol, respectively. It is also noted that the two peaks are relatively narrow.

In Figure 3, model results are presented which incorporate surface heterogeneity, modeled as presented above, *plus* secondary reactions via [R.1], for the same three heating rates used in Figure 2. As can be ascertained from this figure, save for the high temperature shoulder on the CO peak (an effect which is not included in the model), these results are quite similar to the experimental spectra presented in Figure 1, especially, of course, the one calculated for a heating rate of 100K/min. Obviously, surface heterogeneity broadens the features considerably. Also, the sensitivity to heating rate is still evident.

Our experimental TPDs do not exhibit as much sensitivity to heating rate as those shown in the model results of Figures 2 and 3. Some sample experimental TPDs are presented in Figures 4 and 5. Although Figure 4 for the Stockton-Lewiston coal char does exhibit some variation of the major CO peak temperature with heating rate, the Pittsburgh #8 coal char shows practically none. Therefore, at this point we are still unsure as to whether surface heterogeneity can entirely account for this experimentally observed behavior, and/or whether the fundamental assumption concerning first order desorption is in error.

In any case, the major striking feature of Figure 3 is the appearance of a second CO₂ "reflection" peak under the major CO desorption peak, which is obviously due to secondary reaction via the forward step of [R.1]. In fact, in all our extensive experimental TPD data on porous coal chars, we have never observed a CO peak ca. 1000K without also observing a "reflection" CO₂ peak. The "reflection" peak in Figure 3 decays with significantly greater "tailing" than the CO peak. That this "tailing" is not due to diffusional resistance is evident by comparison with the first CO₂ peak which does not "tail" very much at all, under the conditions assumed. It is also noted that in order to produce the "reflection" peak, the reverse step of [R.1] must also be included. If this is not done, the rate of conversion to CO will increase much more rapidly with temperature since the rate constant is assumed to be Arrhenius temperature dependent. Under these conditions, the conversion of CO will continue unabated until all the surface complex is exhausted. The reverse reaction is also required by the principle of microscopic reversibility.

Figure 6 presents model results obtained by varying the diffusion time, t_d . As can be seen, increasing the diffusion time over the range examined, by increasing t_d from 2 to 200 s, does not appreciably increase "tailing" of the "primary" CO₂ and CO peaks. However, the degree of secondary reaction is quite sensitive to the diffusion time. The higher the diffusion time, the greater the conversion of free CO to CO₂ via [R.1], as manifested by a decreasing "primary" CO peak, and an increasing "secondary" CO₂ peak; by $t_d = 200$ s, the "secondary" CO₂ peak is *greater* than the "primary" CO peak in this calculation. In addition, it is interesting to note that the "secondary" CO₂ peak progressively shifts to lower temperature, while the primary CO peak shifts to higher temperature with increasing degree of secondary reaction. In fact, for $t_d = 200$ s, the "secondary" CO₂ peak crosses the "primary" CO peak. This type of behavior has also been noted experimentally in our coal char TPDs. One such representative set of results for Wyodak coal char is shown in Figure 7.

The enhancement of secondary reaction with increasing t_d is due, of course, to the fact that increased intrapore residence time favors the conversion of free CO to CO₂ via [R.1]. The degree of secondary reaction is primarily dependent on three variables: the concentration of intrapore CO; [CO] surface complex coverage; and intrapore residence time. Although we have not yet shown it with the model, we believe that the maximum in net CO₂ production with heating rate [4] is a manifestation of this effect. That is, at low heating rates the amount of CO₂ increases with heating rate, as occurs in Figure 6, since higher temperatures are achieved at high enough intrapore concentrations to enhance CO₂ formation via [R.1]. However, at some point, the intrapore residence time becomes low enough due to the large intrapore gradients induced by rapid desorption, and perhaps enhanced by rapid activated diffusion, that intrapore concentrations begin to progressively decrease by the time the appropriate temperature range is attained in the course of the TPD. The resultant effect is to decrease the net amount of CO₂ produced beyond this point - hence the maximum.

Conclusions

The preceding has shown that a numerical model of the TPD behavior of surface oxygen complexes is a very useful tool for aiding in the interpretation of experimental TPD data. The fact that secondary reaction via [R.1] contributes significantly to the spectra, in terms of CO₂ "reflection" peaks and diminution of the primary CO peak, shows that it becomes a very important consideration under the appropriate conditions. The fact that the degree of secondary reaction has been found to be very sensitive to the kinetic parameters, energetic heterogeneity via the activation energy variation with surface coverage, and the diffusion time may help explain the significant *quantitative* variations in TPD spectra obtained by different workers on various chars and carbons. In fact, it may be possible to develop the sensitivity of secondary reaction to intrapore diffusivity into a technique for measuring transport rates. Diffusional resistances of the order-of-magnitude examined here do not seem to contribute appreciably to "tailing" and broadening of the primary desorption peaks; surface heterogeneity seems to be primarily responsible for the latter. This result will be used to obtain a measure of the energetic heterogeneity of coal chars under varying conditions. The model will be the primary tool in this regard. Recently, we have also begun to incorporate CO re-adsorption onto high-energy sites during the course of TPD, in order to model the high temperature shoulder, which, under certain circumstances, we have observed develop into a separate CO peak, the appearance of which varies considerably depending on various conditions. This mechanism represents another secondary interaction effect with the char surface that occurs during TPD that must be taken into account in order to properly deconvolute TPD spectra of oxygen complexes from coal chars.

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Table I. "Base case" parameter values.

$k_{1d,0}, k_{2d,0}$	kT/h	s^{-1}
k_{10}	3.14×10^{18}	$cm^3/mol \cdot s$
$k_{2,0}$	1.25×10^{22}	$cm^3/mol \cdot s$
$E_{1d,0}, \alpha$	73.0, 10.0	kcal/mol
$E_{1d,0}, \beta$	41.0, 100.0	kcal/mol
$R^2/D_{1,0}$	2 ⁽¹⁾	s
$D_{2,0}/D_{1,0}$	7 ⁽¹⁾	-
E_{d1}, E_{d2}	2 ⁽¹⁾	kcal/mol
C_t	2.5×10^{-5}	mol/cm ³ ⁽²⁾
ϵ	0.3	-
B	1.67	K/s
$E_{1,0}, \gamma$	74.0 ⁽³⁾ , 20.0	kcal/mol
$E_{2,0}, \delta$	99.0 ⁽³⁾ , 10.0	kcal/mol

(1) Estimated from Ref. [9].

(2) mol active sites/cm³ of microporous carbon region.

(3) Obtained from Ref. [10].

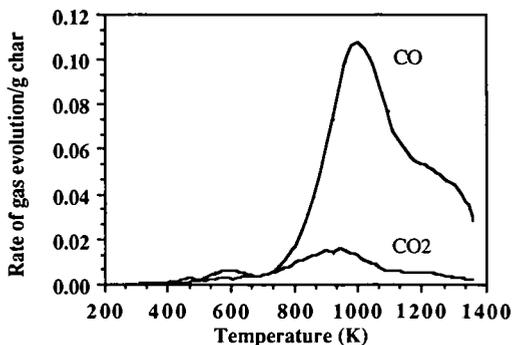


Figure 1. Experimental TPD spectra of Pittsburgh #8 coal char gasified to 27.3% burn-off in 0.1MPa of oxygen at 723K; taken at 100K/min.

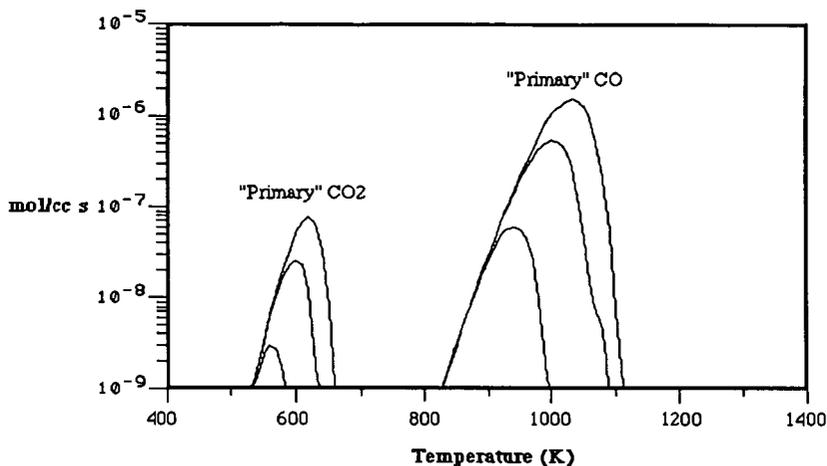


Figure 2. Model TPD spectra for two types of homogeneous complexes (i.e.; CO_2 - and CO -liberating), at three heating rates: 300K/min; 100K/min; and 30K/min. The higher heating rate corresponds to the larger peak in each case. The activation energies for the 600K and 1000K peaks are 38.3 and 66.7 kcal/mol, respectively. The logarithmic ordinate scale is used to present all three cases conveniently on one plot.

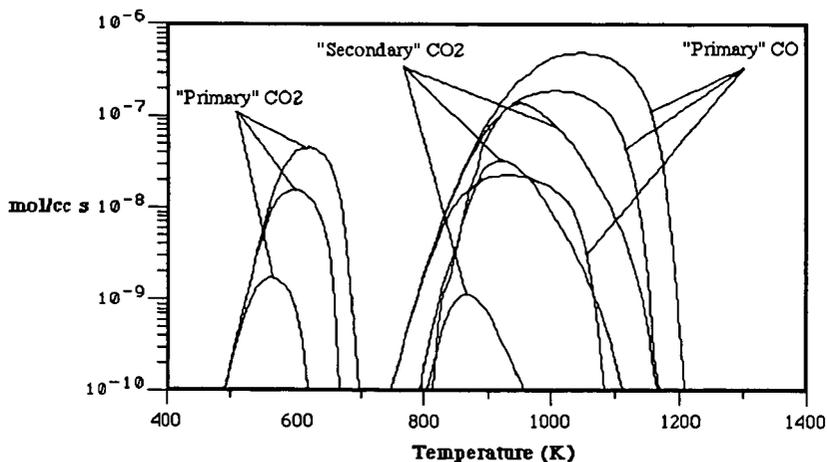


Figure 3. Model TPD spectra, including surface heterogeneity and secondary reaction via [R.1], for the "base case" parameter set listed in Table I, for three heating rates: 300K/min; 100K/min; and 30K/min. The higher heating rate corresponds to the larger peak in each case. The logarithmic ordinate scale is used to present all three cases conveniently on one plot.

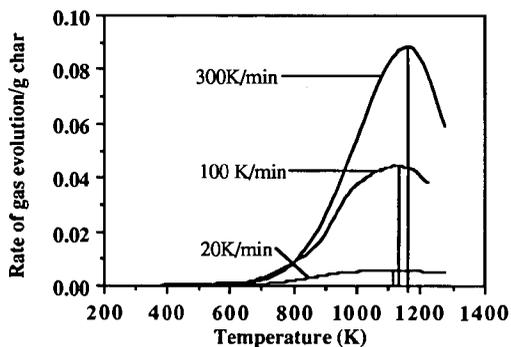


Figure 4. Experimental CO TPD spectra for Stockton-Lewiston coal char after chemisorption for twelve hours in 0.1MPa of oxygen at 523K at heating rates of 300K/min, 100K/min, and 20K/min.

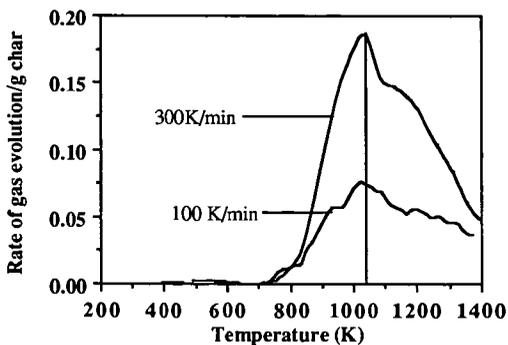


Figure 5. Experimental CO TPD spectra for Pittsburgh #8 coal char gasified to 10% burn-off in 0.1MPa of oxygen at 823K at heating rates of 300K/min and 100K/min.

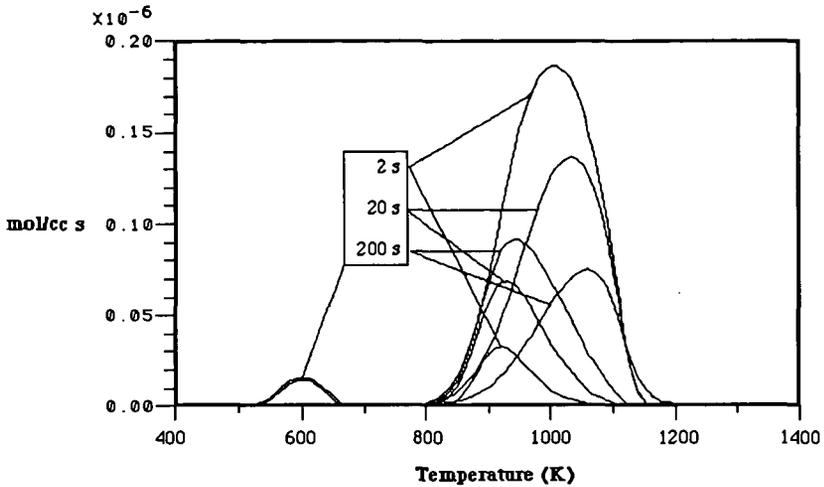


Figure 6. Model TPD spectra, including surface heterogeneity and secondary reaction via [R.1], for the "base case" parameter set listed in Table I with diffusion times of 2, 20, and 200 s.

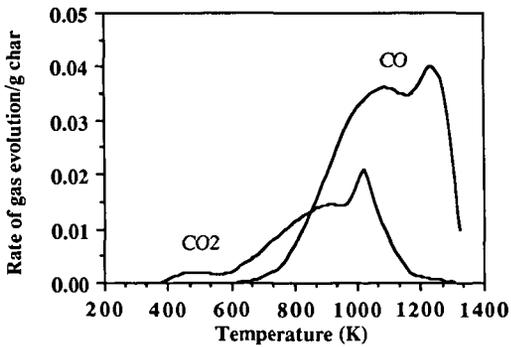


Figure 7. Experimental TPD spectra of ungasified Wyodak coal char exposed to 0.1MPa of oxygen at 573K for twelve hours; taken at 100K/min.