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KINETICS AND MECHANISMS OF NO_x - CHAR REDUCTION

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1.0 Introduction

This report conveys recent progress on two issues. The first concerns the prediction of char-NO reactivity in general. The work has been performed based upon a literature review, supplemented by our own recent results. The second part has to do with more detailed issues related to the mechanism of the reaction. Specifically, it is concerned with how oxide desorption can affect the observed kinetics.

The report is divided into two stand-alone sections, on each of the above two topics. This material recently served as a basis for two manuscripts prepared for presentation at the upcoming American Chemical Society National meeting.

2.0 A Comparison Of The Reactivities Of Different Carbons For Nitric Oxide Reduction

2.1 General Background

Carbon has been recognized to play a significant role in reducing NO in some combustion systems (e.g., fluidized beds) and offers the potential as a reducing agent in other, new applications. In order to more fully appreciate this potential, it is useful to explore what factors influence the reactivity of carbons (and, more generally, chars) towards NO. This section summarizes what is known about the reactivity of different carbons, and examines some questions raised by the comparison, in light of new experimental results.

The reduction of NO by carbons may, for simplicity, be represented by the general reaction:

Other products (for example, N_2O) are possible under certain specific conditions. Likewise, other reaction pathways (involving carbon catalyzed NO reduction by CO) are

also possible. Still, the main carbon reduction route involves the products as indicated. Many aspects of this reaction system have been reviewed in recent years [e.g., 1-4]. Many of the published data on the NO-carbon reaction are summarized in Figures 1 and 2. A more complete summary of the available data is in preparation, and will be presented shortly. This summary is intended to convey the essential features of what is known about the kinetics of the reaction.

Figure 1 presents the data on the rate constant for the reaction, expressed as an NO consumption rate, on a per unit mass of carbon basis. The assumption has been made, consistent with most reports in the literature, that the reaction is first order with respect to NO [1,2, 5- 8]. Several features are immediately apparent. First, there is a significant spread in the rates of reaction. The variation is of two to three orders of magnitude, which may not initially be surprising inasmuch as the data were not normalized based on surface areas, *vide infra*. It is apparent that there is quite commonly a shift in apparent activation energy of the rate constant. The "breaks" occur at temperatures ranging from about 900 to 1050 K, and always involve an increase in activation energy with increasing temperature. This break has been earlier noted by several groups. It must involve a change in mechanism, as opposed to an encroachment of heat and/or mass transfer effects, since the shift is in the direction of higher activation energies with increasing temperature. A hypothesis to explain the two regimes has been previously advanced [2]. The individual studies offer a wide range of activation energies, with some sets showing no evidence of the "break". There are surprisingly few clear trends with the nature of the carbon. For example, a highly pyrolyzed resin char exhibits a lower reactivity than does a graphite. De-ashing of a lignite char shows only a modest effect on reactivity. A cellulose char with low inorganic impurity content is seen to have a higher reactivity than coal chars.

Figure 2 presents a comparison of literature data on a surface area-normalized basis. The surface areas were taken as reported by the investigators themselves, and include some measured by nitrogen sorption and others with carbon dioxide. It should be noted that the data sets represented in Figures 1 and 2 are not identical, because the data were not always

available to include results on both plots. It is perhaps surprising that converting data to a surface area basis does little to reduce the amount of scatter in the data. It is worth noting that the degree of scatter is not unlike that observed in similar summary plots of data on the oxygen-carbon reaction [9]. Thus it appears as though there is a high degree of variability of carbon reactivity towards NO, just as there is towards oxygen. This has been attributed to differences in the numbers of active sites per unit surface area. It is not yet possible to predict this value. It is interesting to note that the graphites exhibit relatively high reactivities per unit surface area. There is, however, no clear trend in reactivity with the nature of the carbon.

The results of Figures 1 and 2 present a confusing picture of the factors that influence the reactivity of carbons towards NO. While small subsets of the data can be compared and logical hypotheses drawn regarding the influence of certain variables, there is not yet an ability to predict reactivity to better than orders of magnitude uncertainty. The problem with an approach based upon comparing reactivities from literature accounts is that there are a number of experimental variables that may have had an influence on reactivity, and these are never completely controlled or reported. Most of these variables have to do with how the carbon is prepared, but some might also have to do with how the reactivities were determined. The remainder of this section will explore how measured reactivities can be influenced by a number of experimental factors.

2.2 EXPERIMENTAL

Two different reactor systems were selected for study, in order to represent the two most widely employed techniques for study of this reaction. The first reactor system was a thermogravimetric analyzer (TGA). In this case, a TA Instruments TGA was employed. As compared with the Cahn TGA system in which we had performed most of our earlier work [1,2], the TA Instruments TGA has a somewhat smaller enclosed gas volume. Thus, the experiments were performed with a continuous gas flow through the TGA to ensure that depletion of NO was not significant. The TGA work was performed, as earlier [1,2], at

quite high NO partial pressures, ranging from about 1 to 10 kPa of NO partial pressure.

Many of the studies reported in the literature have employed packed bed reactors. One of the advantages of these systems is that they more realistically simulate possible "end-of-pipe" reduction systems. They also tend to be less complicated to operate, allowing for a steady flow of NO-containing gas which is continuously analyzed using an NO_x analyzer. Operation at lower, more realistic, NO concentrations is also possible. Operation of a TGA at low NO concentrations is often considered impractical, because of the long times needed to achieve significant burnoff (weight loss).

In our case, we employed a 4 mm ID packed tubular reactor, made of quartz. A bed of between 20 and 200 mg of carbon (char) was packed into a predetermined length of between 1 and 30 mm, depending upon the conditions to be studied. The bed was held in place with quartz wool. Blank runs indicated no significant NO reduction in the absence of carbon (this was not the case if ordinary glass wool was employed). A carrier flowrate between 70 and 125 cc/min of helium was passed through the reactor. In the work considered here, the only other component in the inlet gas was NO. The inlet NO concentration ranged between 100 and 300 ppm. The particle size in the bed was approximately 200 μm in all cases. Before all runs, the surface of the char was cleaned of oxides by heating at 1173 K for one to two hours.

2.3 RESULTS AND DISCUSSION

Several different carbons were tested in the TGA, using a consistent protocol. The samples examined were a resin char (ex-phenolformaldehyde) that we had earlier extensively studied [1,2], a graphite powder (from AESAR/Johnson Matthey Company), a coconut char (from Fisher Scientific), and a Wyodak coal char, prepared from a sample obtained from the Argonne Premium Coal Sample Program. The results are shown in Figure 3.

The results of Figure 3 show that this wide range of carbons gives fairly consistent rates, when the results are represented on a unit surface area basis. The one exception is the

rates from our earlier work [1,2], and the reasons for this will be discussed below. It should be noted that the carbons range from those of quite high purity (the phenolic resin char and the graphite) to a mineral-containing coal char. The good agreement between the carbons and chars might be attributable to the fact that an effort was made to compare highly heat treated materials, in this case. The coconut char and graphite were used as-received (apart from surface cleaning at 1273 K for one hour). The phenolic resin char and the Wyodak char were prepared by a two-hour pyrolysis at 1223 K, and then surface cleaned prior to use. Thus for carbons and chars which may be considered as "old" there is quite good agreement in reactivity. Further tests, which will be reported separately, have not surprisingly indicated that the "age" of a char (i.e., how severely it is heat treated) does indeed have some effect on its reactivity. Here, however, it came as a surprise that the aging seems to lead to similar reactivities towards pure NO, despite significant differences in contents of impurities.

Figure 3 also indicates that the "break" in the Arrhenius plots depends upon the type of carbon. It can be seen that the break occurs at a much higher temperature in the graphite than in the other carbons. The agreement between the reactivities of the different carbons, on a per unit mass basis, was not nearly as good. In fact, the results gave a spread similar to that seen in Figure 1. Thus it appears that the reactions occur in Zone I, and that the micropore area of the carbons is significant.

When our earlier TGA results on the same resin char are compared with those from the present study, there appears to be a significant difference (see Figure 3). This turned out to be a consequence of how the sample was prepared, and indicates an important consideration in developing experimental testing procedures. The extent to which the resin char surface was cleaned of oxides was responsible for the differences in the observed rates. In our earlier work [1,2], the reactivity of the resin char was established as a function of temperature, merely by varying temperature and recording what appeared to be pseudo-constant rates. This might be considered a "normal" experimental procedure. In this more recent work, it was learned that by cleaning the surface of oxides, by heating at 1273 K for

an hour between each temperature to be studied, the resulting pseudo-steady mass loss rate was significantly higher. This means that the oxide population on the char surface is a function of the reaction history of the sample, and that this, in turn, influences the observed rate. What may appear to be a pseudo-steady state rate might actually be slowly evolving, as the oxide population readjusts on a timescale longer than that used to obtain the rate. We had actually noted the same problem earlier, in connection with determination of the reaction order with respect to NO [1]. Failure to clean the surface between different partial pressures gave an apparently less than unit order with respect to NO, since the surface oxide population could only very slowly adjust to the new NO partial pressure. Thus it is essential to report how kinetic experiments are performed, in order to establish a sample reaction history. Without this information, comparison of rate data from the literature may be quite misleading. Once this aspect of the process was noted, all our experiments were performed on a self-consistent basis, with surface oxide cleaning between each temperature step. Because we are measuring rates on a virgin surface in each case, issues related to the influence of remaining oxides on rate are minimized. Further experiments in the TGA again established that the reaction is unequivocally first order with respect to NO partial pressure, validating the form of the rate constant used in Figures 1 through 3 (see Figure 4).

Generally, good agreement was obtained between the rate constants from the TGA and packed bed experiments, despite the fact that there was about a two order of magnitude difference in the concentrations of NO in the two reactor systems (around 2% in the TGA vs. 200 ppm in the packed bed reactor). Results for the coconut char in Figure 5, illustrate this conclusion. Further discussion of the small differences will be presented elsewhere. Thus apparently large differences in reactivity in Figures 1 and 2 are not attributable to what type of reactor system is used for testing, nor to the concentration level of NO employed. It is clear that the purity of the gas feed is important in determining the apparent reactivity; small amounts of oxygen affect rates significantly. This will be reported on elsewhere. We have further established, consistent with an earlier presented hypothesis [10], that it is difficult to obtain reliable reaction order information from packed bed experiments. This

will also be reported at a later time.

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Figure 1. NO-carbon reaction rate constant, per unit mass of carbon reactant.

Figure 2. NO-carbon reaction rate constant expressed on a surface area basis

Figure 3. NO-carbon reaction rates from TGA experiments.

Figure 4. Reaction rate of resin char in the TGA, showing first order rate. ($T=600^{\circ}\text{C}$)

Figure 5. Comparison of rates obtained on various samples, in the TGA and packed bed reactor.

3.0 An Examination Of The Two Kinetic Regimes Of The Nitric Oxide-Carbon Gasification Reaction

3.1 Background

The reaction of NO with carbon has been shown by many workers to involve two distinct rate regimes, at temperatures of practical interest [1,2]. Based upon our earlier results, we suggested that the two regimes most likely involve rate control by site creation in the low temperature regime and dissociative chemisorption in the high temperature regime. Further experiments and analysis will be presented here in support of these hypotheses.

The mechanism of the NO-carbon reaction has been suggested to involve the following steps [2]:

The reaction (R3) is only important at quite low temperatures ($< 473\text{K}$) [4]. The reactions (R1) and (R2) are dissociative chemisorption on non-rapid turnover sites [2]. The reactions involving C^* are the rapid turnover site reactions, that yield both CO via (R5) and CO_2 via (R4). The reaction (R2) allows for some small amounts of stable CO_2 -forming complex on the surface. The reactions (R6), (R7) and (R8) reflect formation of empty rapid turnover sites C^* , as well as non-rapid turnover sites, C. The exact nature of the C^* sites and C

sites, and what makes them different, is unclear. Thus the stoichiometry of their formation is also unclear. The reactions (R6)-(R8) are governed by distributions of activation energies, and (R6) and (R7) make a large contribution to the overall rate at low temperatures [1,2]. In fact, the rapid turnover processes (R4) and (R5) are probably governed by the same continuum of activation energies as are (R7) and (R6), respectively, except that at any given temperature, certain sites are effectively immediately desorbed upon formation.

The low desorption activation energy surface species, for which the rate of desorption is quite fast compared to the rate of their formation by dissociative chemisorption of NO, give rise to surface sites that are normally "empty" (the C* sites). Again, it is probably impossible at the present time to define a particular reaction pathway for a particular type of site. The concept of a rapid turnover site is largely a bookkeeping construct. Without direct evidence to support the view that there exists a particular carbon structure C* which will, upon oxidation, immediately desorb as part of CO or CO₂, it is more prudent to adopt a more flexible view of what C* might represent. It may well be the case that chemisorption on one surface site will tend to destabilize another, neighboring oxide structure. This view is supported by the recent insightful isotope labeling experiments of Orikasa et al. [5], which suggested that the rate of (R6) might be enhanced by processes involving participation by NO itself (though a thermal artifact was seemingly not ruled out). Kinetically, the transient behavior observed by these workers at 873 K appeared consistent with a rapid turnover process such as (R5), and the isotopic composition showed that some of the oxygen came from oxide on the surface [5]. Thus it might be necessary to define C* more broadly, so as to include not only a carbon structure that is able to be oxidized, but also possibly neighboring carbon oxide sites. A similar suggestion has been advanced by Tomita and coworkers [6,7]. This represents a considerable step in the direction of increasing complexity of models of the oxidation process.

Here, we consider some new experimental results that help to shed further light on models of NO reaction with carbon. In particular, we explore further the role of surface oxides in determining the rate of the reaction processes in both the high and low temperature regimes. These two regimes have been discussed elsewhere [1,2], and typical two-temperature regime behavior is seen in Figure 6, which will be discussed below.

3.2 EXPERIMENTAL

Two different thermogravimetric analyzer (TGA) reactor systems have been used in this study; one from TA Instruments and the other from Cahn Instruments. The TA Instruments TGA has a somewhat smaller enclosed gas volume than does the Cahn system, thus, the experiments in the TA Instruments TGA were performed with a continuous gas flow through the TGA to ensure that depletion of NO was not significant. Apart from this small difference, the TGA work was performed as earlier described [1,2], and the results indicate no significant differences attributable to the particular TGA system used. As is usual in our TGA work, experiments were performed at quite high NO partial pressures, ranging from about 1 to 10 kPa of NO partial pressure. The reaction has been shown to be first order in NO over a very wide range of pressures [3], and the rates from this range of pressures can be extrapolated with confidence to lower partial pressures.

Some experiments were performed in a packed bed reactor system. This reactor consisted of a 4 mm ID quartz tube packed with around 100-200 mg of char, giving a bed length of order 10-30 mm. The NO concentrations examined in this system were much lower than those in the TGA system, and ranged from about 1 to 20 Pa.

One material selected for study is a char derived from phenol-formaldehyde resin. It has been described before [1,2]. This material has a relatively low impurity content. The material has been heat treated at 1323 K for two hours prior to any experiments. A second material is a char derived from Wyodak coal char. This char was derived from a sample of the Argonne Premium Coal Sample Program [8]. Details of its pyrolysis will be discussed

below.

The chars were also subjected to "surface cleaning" in some cases. This procedure involves exposure of the char to high-pressure flowing helium at either 1223 or 1273 K for one to two hours. This results in removal of most, though not all, of the desorbable oxides from the surface. The amount of surface oxides that remains after surface cleaning is difficult to establish, quantitatively. The rate of oxide desorption at the end of the the surface cleaning process is generally quite low, when the process is stopped.

3.3 Results and Discussion

3.3.1 Factors Affecting the Active Site Concentration

Typical results of the experiments on the resin char, at an NO partial pressure of 2 kPa, are shown in Figure 6. The results are shown as first order rate constants for the destruction of NO on the carbon surface. The data show the previously discussed two-temperature-regime behavior. Two different types of experiments are shown and both show the two-regime behavior. One set was performed as previously described [1,2]. Samples were subjected to a sequence of different temperatures, under a constant NO partial pressure. Different temperatures were explored by simply changing the temperature of the reactor. To hasten achievement of pseudo-steady state behavior, these experiments were performed by starting the experimental sequence at high temperatures. No attempt was made to clean the surface of oxides between each temperature step. These experiments will be referred to as those involving an "uncleaned" surface. These experiments gave relatively constant rates of mass loss (the main experimentally measured quantity) over timescales of tens of minutes, and these are what are reported in Figure 6. The approach to apparent steady state was generally faster, the higher the temperature.

A second set of experiments was performed with an identical material, but with a different experimental procedure. The difference had to do with how the surface was prepared for an experiment. Rather than permitting the oxides to remain on the surface

throughout the experimental sequence, in this case, each time the temperature was changed, the oxides were desorbed (to a significant extent) by heating the sample at 1223 K for two hours. These experiments are described as involving a "cleaned" surface. This somewhat more tedious experimental procedure had been earlier followed in experiments designed to determine the true order of reaction [1]. In that case, it had been observed that leaving the oxides on the surface gave an apparent non-unity order with respect to NO, particularly in the high temperature regime. This was because the timescale for the oxide population to adjust itself to a different pressure was sufficiently long (many hours) that it was easy to miss this fact in experiments in which the appearance of linear mass loss with time was used to judge approach to pseudo-steady state. In the experiments reported here, the rates were again taken to be those at apparent pseudo-steady state, consistent with how the rates were determined for the uncleaned samples.

Comparison of the results of experiments with cleaned and uncleaned samples shows that in the low temperature regime (below about 1000 K), the rate of the reaction is clearly higher with the surface cleaned samples. In the high temperature regime, no significant differences have been noted between cleaned and uncleaned samples in these, or any other, experiments. Thus there is suggestion that the existence of oxides on the surface can retard the apparent rate of the gasification under certain circumstances, commensurate with the above model in which the C^* is viewed as depending upon free sites for rapid turnover [2]. It should be noted that this result is not a consequence of "thermal annealing" [9], in that the more highly heat treated carbon (that with the surface cleaned after each cycle) is more reactive than the sample for which this is not done. These results at first appear to be in direct contradiction to those reported by Suzuki et al. [7], in which oxidation of a carbon surface enhanced the rate of reaction with NO. It is possible that the discrepancy arises from the different degree or nature of oxidation (or surface cleaning) in the two studies. Suzuki et al. used O_2 to oxidize the surface, and the complexes created by oxygen may be different than those created by NO. We have seen evidence of this difference in TPD studies. Further, it has been noted by Tian [10] that addition of H_2 to an

NO containing mixture increases the rate of NO destruction. Tian's experiments were conducted at 1073 K, and appeared to be in what we term the high temperature regime, so it is unclear that they can be compared directly with the present results. Nevertheless, they are clearly suggestive of a role of oxide removal in rate enhancement.

Similar types of experiments have been performed at significantly lower NO partial pressures in the packed bed reactor. The effect of surface cleaning is barely visible (and of course the overall reaction rates are much lower). This means that the effect of surface oxide population is associated with the partial pressure of NO. The pseudo-steady population of surface oxides increases with increase in NO pressure, though this dependence is very weak at high NO pressures [1], possibly indicating surface saturation. There is, however, evidence that the reaction shows a higher order dependence upon NO pressures when NO pressures become low (of order 1 Pa). This would be expected, as reactions such as (R2) and (R4) become "starved" for surface oxides. The concentration of surface oxides would be expected to become more sensitive to the NO pressure, as the pressure of NO is decreased (as may be reasoned from a simple Langmuir-type adsorption model).

We have also studied the effect of differences in active site density in another way, as shown in Figure 7. This figure illustrates the effect of heat treatment on Wyodak coal char. One char was prepared by heating at 1273 K for a total of four hours, while the other was heated up to a temperature of 1273 K, at a rate of 30 K/min, and then immediately cooled. The results of Figure 2 show one facet consistent with what was seen in Figure 6 - the effects of heat treatment are most notable in the low temperature regime, and largely disappear in the high temperature regime. Here, however, the less highly heat-treated char, which presumably contains more active sites to begin with, was not surface cleaned during the experimental sequence (in fact, each point was obtained with a "fresh" sample). The more highly heat treated char was surface cleaned. The less highly heat treated material would have had more active sites to begin with, and would have retained these, but for filling with oxides. The change in the population of sites with time was not explored. Thus

the conclusion from these experiments is that thermal annealing effects can and do play the usual sort of role in influencing reactivity, but the effects are different in the two temperature regimes. It may be further concluded, by comparing with Figure 6, that surface cleaning may affect the extent of annealing, but by the time a sample has already been heat-treated for several hours at 1273 K, the annealing effects become less important than the site-blockage effects.

There are two general conclusions which may be drawn based upon these results. The first is that examination of the rates and dynamics of the NO-carbon reaction must always establish in which temperature regime the processes of interest are occurring. There is no possibility of deriving "general" conclusions concerning mechanism without careful consideration of this point. There is ample evidence of very long timescale dynamics associated with rearrangement of surface oxides, which, in turn, can significantly affect the observed rates. The effects of NO partial pressure must also be taken into account. The second general conclusion is that the rates in the low temperature regime appear to be generally more sensitive to any factors that affect active site populations than are rates in the high temperature regime. It is already clear that the process of NO destruction (or gasification) is somehow different at the higher temperatures. It is possible that a different set of active sites begins to dominate the rate because a different reaction pathway becomes favorable, or it might be that as a result of an increase in available active sites, a second step in a reaction pathway becomes limiting. We have earlier suggested this latter possibility [2].

3.3.2 The Kinetic Role of The Rapid Turnover Active Site Population

The relative roles of the desorption processes such as (R6) compared to the rapid turnover processes such as (R5) has been earlier examined, using the resin char [2]. The rate of carbon gasification is given by the sum of contributions from the desorption processes and the processes such as (R5): $r = r_a + r_d$, where r_d corresponds to (R6) and r_a to (R5). The focus on CO-yielding reactions is chosen for simplicity; the analysis may be extended to include CO₂ as a product as well, at the expense of greater complexity. The

data on the overall rate, r , and the desorption rate in the absence of NO, r_d , have been given elsewhere [2]. Noting that $r_a = k_a[C^*]P_{NO}$ and $r_d = k_d[C(O)]$, then it can be seen that:

$$d[\ln(r_a/r_d)]/d[1/T] = -(E_a - E_d)/R + d \ln [C_{tot}/C^* - 1] / d [1/T]$$

where C_{tot} is the total number of sites in either the form C^* or $C(O)$. Working at the limit $C^*/C_{tot} \ll 1$, i.e., most sites are oxide-filled, allows the above result to be approximated as:

$$d[\ln(r_a/r_d)]/d[1/T] = -(E_a - E_d)/R - d \ln [C^*] / d [1/T]$$

The left hand side of the above equation is shown in Figure 8, yielding a slope of - 3969 K. The value of the last term on the right hand side is evaluated from experiments in which the free sites are filled at a temperature below gasification (see ref. 2). The result is also seen in Fig. 8, and define a slope with $(1/T)$ of -7100 K. The rate of desorption of oxides from the surface was tracked in TGA experiments in which the mass loss rate was followed after removal of NO [1,2]. These data are represented in Figure 9, yielding an apparent $E_d = 89$ kJ/mol. Combining the above values yields $E_a = 181$ kJ/mol, in good agreement with the experimentally determined value for the high temperature range (e.g., Figure 6).

It is noteworthy that the above calculation spanned both the high and low temperature ranges, using data from each. The results of the kinetic calculation are very much in concert with the earlier conclusion, based upon product analyses, that both (R5) and (R6) type reactions occur in both temperature regimes [2]. The fact that reactions of type (R5) appear to play a significant kinetic role in the low temperature regime cannot be overlooked, even though their inherent activation energy is seen only in the high temperature regime. It is the competition between these reactions, at any particular temperature, that determines the apparent kinetic constants. We have also observed that the shift from low-temperature to high-temperature regimes occurs at widely varying temperatures in different carbons, so it is not possible to make a general statement about which processes may be neglected at what temperatures.

Based upon this analysis, and our earlier results, it is clear that there exists a

population of sites that is "empty" (available for reaction) under all reactive conditions, and at which rapid turnover processes occur with an activation energy characteristic of the high temperature regime. The population of such sites appears to increase with increasing temperature. The numbers of such sites depend upon how the sample was prepared (how highly heat treated it was) and how heavily the surface is oxidized. As the temperature of the surface is raised, the population of empty sites increases (due to desorption of oxides) to such an extent that the rate begins to show the thermal dependence of the decomposition of NO on the sites. This defines the high temperature regime. At lower temperatures, the temperature dependence of the overall rate reflects the temperature dependence of desorption processes, since these not only contribute product via reactions such as (R6), but also free up sites for reactions such as (R5). This model will be formalized in a forthcoming report.

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Figure 6. A comparison of the rate constant for NO reduction by resin char with cleaned surface (open squares) and uncleaned surface (closed squares). The NO pressure was 2 kPa.

Figure 7. The effect of heat treatment upon the reactivity of Wyodak char. The open points are for a sample heated to 1273 K at 30 K/min, and the closed points are for a sample heated for four hours at 1273 K (see text). The NO partial pressure was 10 Pa.

Figure 8. The variation of relative rates of rapid turnover and desorption processes with temperature, and the variation of rapid turnover site population with temperature. Values obtained from TGA experiments at 1 to 10 kPa NO pressure.

Figure 9. Oxide desorption rate, after removal of NO from the TGA.

4. Plans for the Upcoming Quarter

Experiments will be continued, using the packed bed reactor. The NO reduction by CO on char surfaces will be studied further during next quarter. Failure to identify the role of these reactions has been identified as playing a key role in leading to possibly incorrect conclusions concerning the order of the NO-carbon reaction.

Hopefully, the TGA/FTIR system will be ready and some preliminary experiments will be performed with this system.