KINETICS AND MECHANISMS OF NO\textsubscript{x} - CHAR REDUCTION

E. M. SUUBERG (PRINCIPAL INVESTIGATOR)
W.D. LILLY (STAFF)
I. AARNA (Ph.D. STUDENT)

DIVISION OF ENGINEERING
BROWN UNIVERSITY
PROVIDENCE, RI 02912
TEL. (401) 863-1420

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P.O. BOX 10940
PITTSBURGH, PA 15236

DR. ROBERT GROSS
TECHNICAL PROJECT OFFICER

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1.0 Introduction

The emission of nitrogen oxides from combustion of coal remains a problem of considerable interest, whether the concern is with acid rain, stratospheric ozone chemistry, or "greenhouse" gases. Whereas earlier the concern was focused mainly on NO (as a primary combustion product) and to a lesser extent NO$_2$ (since it is mainly a secondary product of combustion, e.g. see ref. 1), in recent years the emissions of N$_2$O have also captured considerable attention$^{2-8}$, particularly in the context of fluidized bed combustion, in which the problem appears to be most acute. The research community has only recently begun to take solid hold on the N$_2$O problem. This is in part because earlier estimates of the importance of N$_2$O in combustion processes were clouded by artifacts in sampling which have now been resolved$^9$. This project is concerned with the mechanism of reduction of both NO and N$_2$O by carbons.

It was recognized some years ago that NO formed during fluidized bed coal combustion can be heterogeneously reduced in-situ by the carbonaceous solid intermediates of combustion$^{10}$. This has been recently supplemented by the knowledge that heterogeneous reaction with carbon can also play an important role in reducing emissions of N$_2$O$^{2,6,7}$, but that the NO-carbon reactions might also contribute to formation of N$_2$O$^{2,8}$. The precise role of carbon in N$_2$O reduction and formation has yet to be established, since in one case the authors of a recent study were compelled to comment that "the basic knowledge of N$_2$O formation and reduction still has to be improved"$^8$. The same can be said of the NO-carbon system.

Interest in the NO- and N$_2$O-char reactions has been significant in connection with both combustor modeling, as well as in design of post-combustion NO$_x$ control strategies. As in the case of the NO-char reactions, the reaction of N$_2$O with char is probably too slow to be of significance in dilute particle phase, short residence time, pulverized coal combustion environments$^3$. The suggestion has been made that the reactions could still be important within the pore structure of the coals, even in a pulverized firing environment$^{11}$. The possibility of reburning combustion gases in the presence of fresh coal or char also exists.
The above chemical processes are, however, unquestionably important in the lower temperature, slower reaction rate regime of fluidized beds\(^8\). Of course, it is also the lower temperatures of fluidized bed systems that lead to release of greater amounts of N\(_2\)O from these systems, since the N\(_2\)O destruction processes have higher activation energies than do formation processes\(^7\). Therefore, there remains a significant incentive for studies of these reactions associated with developing better control strategies associated with fluidized bed technologies.

Beyond the applicability of this chemistry in fluidized beds, there is interest in developing new post-combustion processes to control NO\(_x\) emissions. The possibility of using carbons in the role of catalysts for the catalytic DeNO\(_x\)-type processes has been explored\(^{12}\). Their possible roles as catalyst supports has also been examined\(^{13,14}\). The use of activated carbons for NO removal has been studied\(^{12,15,16}\). And as noted above, the use of carbons, with various kinds of catalytic promoters, has been suggested as holding some promise for lowering the useful temperature range of the reduction processes into that of interest for post-combustion processing\(^{17,18,19,20}\). Interestingly, it was even suggested a few years ago that even spent oil shale, which contains char in a largely limestone matrix, could be an effective material for reduction of NO\(^{21,22}\).

2.0 Reduction of NO by Carbon at High Temperatures

The mechanisms of the reactions of carbons with O\(_2\), CO\(_2\), and H\(_2\)O are not yet well understood in many respects. The reactions of carbons with NO are even less well characterized (here, the term "carbons" is used in a generic sense, and interchangeably with the term "chars"). There have been a modest number of studies of various aspects of the NO-char gasification reaction in the last 30 years\(^{17-19,23-41}\). The literature on chars from coals and those derived from other materials show no significant differences, in terms of the trends reported here, though there are large differences in rates, as may be noted from Figure 1 and 2. Also, catalytic effects certainly exist (e.g. ref. 32,18,19), and these will be separately considered below.

Heterogeneous reactions of NO with chars can reduce NO to N\(_2\) and form CO and CO\(_2\) gaseous products. There are two kinetically distinct regimes of NO-char steady state gasification
reactions, as illustrated in Figure 1 and 2. The temperature dependence of the rate of the NO-char reaction from our previous studies\textsuperscript{36,37} and the literature\textsuperscript{28,32,33}, is shown in Fig. 1 and 2. The data of Figure 1 and 2 were obtained on an enormous variety of carbons under a great variety of experimental conditions, so the change in mechanism observed at around 650°C (923 K) is a general phenomenon. All of the kinetic data can only be explained by a rather involved kinetic mechanism. We have proposed a mechanism for the process that includes the following steps\textsuperscript{37}:

\[
\begin{align*}
2 \text{C} + \text{NO} & \rightarrow \text{C(O)} + \text{C(N)} & \text{(R1)} \\
\text{C} + \text{C(O)} + \text{NO} & \rightarrow \text{C(O2)} + \text{C(N)} & \text{(R2)} \\
2 \text{C} + 2 \text{NO} & \leftrightarrow 2 \text{C(NO)} & \text{(R3)} \\
\text{C}^* + \text{C(O)} + \text{NO} & \rightarrow \text{CO}_2 + \text{C(N)} + x\text{C}^* + x'\text{C} & \text{(R4)} \\
\text{C}^* + \text{NO} & \rightarrow \text{CO} + \text{C(N)} + y\text{C}^* + y'\text{C} & \text{(R5)} \\
\text{C(O)} & \rightarrow \text{CO} + a\text{C}^* + a'\text{C} & \text{(R6)} \\
\text{C(O2)} & \rightarrow \text{CO}_2 + b\text{C}^* + b'\text{C} & \text{(R7)} \\
2 \text{C(N)} & \rightarrow \text{N}_2 + d\text{C}^* + d'\text{C} & \text{(R8)}
\end{align*}
\]

In some cases, it might be necessary to include in comprehensive NO-carbon mechanisms a carbon-surface catalyzed oxidation of CO by NO, based upon the observation that NO reduction by carbons is enhanced in the presence of CO\textsuperscript{32,42}. The surface species C(O), C(O2), C(NO) and C(N) are operationally defined by their desorption products (CO, CO2, NO, and N2, respectively) in temperature programmed desorption (TPD) experiments conducted after gasification. The reaction (R3) is only important at quite low temperatures (<473 K). The reactions (R1) and (R2) involve dissociative chemisorption of NO on “non-rapid turnover sites”\textsuperscript{37}, meaning that stable surface oxide species are products of these processes. In contrast to this are the reactions, involving C* as a reactant. These are “rapid turnover site” reactions that yield gaseous products essentially immediately in the temperature range in which high temperature gasification is normally studied. The products of these rapid turnover processes are CO via (R5) and CO2 via (R4). The reactions (R6), (R7) and (R8) reflect formation of empty surface sites, C* and C, together with slow desorption of CO, CO2 and N2. The reactions (R6)-(R8) are governed by distributions of activation energies\textsuperscript{37}. The distributed activation energy desorption reactions (R6) and (R7) make the major contribution to the NO reduction rate at low temperatures (between about 600 and 950 K)\textsuperscript{36,37}. At lower temperatures (<500-600K, depending upon material), the process may not involve the release of gaseous carbon oxides; instead, stable surface oxides are formed on the carbon via chemisorption\textsuperscript{24,43-46} and pseudo-
steady gasification is not observed. We have seen no evidence of reversible desorption of NO via (R3) once it is chemisorbed, except at very low temperatures (below 473 K) \(^{43-46}\), so all NO chemisorption is dissociative under steady reaction conditions.

In fact, the rapid turnover processes (R4) and (R5) are certainly 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, and are here shown separately only for convenience. Very low desorption activation energy surface species (for which the rate of desorption is quite fast compared to the rate of formation by dissociative adsorption of NO) give rise to surface sites that are normally “empty”. These are the “rapid turnover sites”.

A similar mechanism to ours has recently been proposed by Yamashita et al.\(^{19}\), except that they proposed a formal distinction between stable and desorbable carbon oxide sites, and a rearrangement type of conversion between the two. Again, we do not believe that a formal distinction needs to be drawn between desorbable and stable oxide sites, and we do so only for convenience in our model. Where we also disagree with Yamashita et al. is in the fact that (R6) through (R8) must be described by a distribution of activation energies, to correctly describe all known behavior. Finally, Yamashita et al. did not allow for formation of stable nitrogen-containing complexes, which is necessary both during gasification\(^{36}\) and chemisorption\(^{43}\).

It has been noted that the reaction of NO with char parallels in some respects the reaction of \(O_2\) with chars, in that surface oxide intermediates play a key role in the mechanism. Very limited amounts of nitrogen complexes, C(N), can also be formed. It should also be noted that the formation of \(N_2O\) is generally not considered to be significant in the NO reduction process, and this product is not measurable except in what is below termed the "low temperature gasification regime"\(^{36}\). As noted above, formation of \(N_2O\) is, however, important in many fluidized bed coal combustion systems\(^{12}\), but this may or may not be due to NO-carbon reactions.

The reaction of NO with carbons is generally reported to be first order with respect to NO partial pressure\(^{23,24,32,33,36,37}\), in contrast to reactions of carbons with \(O_2\), which typically
exhibit a fractional order\textsuperscript{47}. The ratio of CO to CO\textsubscript{2} in the gasification products of carbon by both O\textsubscript{2}\textsuperscript{48-51} and NO\textsuperscript{24,25,32-34,36} show similar qualitative trends - the ratio increases with increasing temperature.

As noted above, in the case of NO-carbon reactions, there is a significant change in kinetic parameters and, therefore, mechanism at a temperature in the neighborhood of 925 K (actually in the range from 873 to 953K)\textsuperscript{32,33,36,37}. This is inferred from a change in apparent activation energy for the process. The trend of activation energy with temperature is opposite to that which would be expected if this were simply a case of transition from chemical reaction rate control to mass transfer control, because higher activation energies are observed at higher temperatures. The reasons for this behavior were a main focus of our earlier study. The reasons for the change in mechanism will now be summarized.

The low temperature regime of steady NO-carbon reaction (crudely < 925 K) is characterized by a non-constant activation energy in the range of 30-50 kJ/mol not 63 - 88 kJ/mol as was suggested earlier \textsuperscript{36} see Fig. 3. In this regime, there is a significant contribution from the desorption of relatively stable surface complexes, such as (R6) which proceeds without direct involvement of NO in the step. This has been revealed by isothermal desorption experiments, in which the NO was quickly removed from the gaseous environment\textsuperscript{36}. Below 925 K, most of the product CO is released by the process (R6). In contrast to this, CO\textsubscript{2} formation during low temperature gasification apparently requires closely coupled participation of NO in the product release step, via (R2). The rate of this process is controlled by the rate of formation of surface oxide intermediates that are unstable in the low temperature regime of Fig. 1. (These same complexes are, however, stable at lower temperatures, at which only chemisorption occurs, and little carbon oxide formation takes place.) Thus the rate of CO\textsubscript{2} formation is controlled by the chemisorption of NO via (R2), rather than by the rate of desorption of stable complexes, via (R7)\textsuperscript{37}. In the O\textsubscript{2}-char reaction, Perlmutter and coworkers\textsuperscript{52,53} have suggested that a similar situation exists, involving the “direct” burn-off of some “unoccupied” surface, without formation of stable oxide species on the surface i.e.,
\[ C + O_2 \rightarrow CO, CO_2 \] (R9)

The NO-char reaction in the high temperature regime (again, crudely > 925 K) has a constant activation energy of 180kJ/mol\(^3\), and the process is also hypothesized to involve prompt (non-rate-determining) gaseous product release. The process is controlled by the rate of NO reaction with the surface sites, such as by reactions (R1) and (R2), as demonstrated by the fact that the rate of product formation was \textit{unity} with respect to NO, even when CO\(_2\) was a major product\(^3\). This is because total population of all desorbable surface species (mainly composed of C(O)) has been shown to exhibit a weak NO pressure dependence of \((P_{NO})^{0.16}\) at 973K and \((P_{NO})^{0.08}\) at 1073K. The rate of CO\(_2\) formation is proportional to both the gas phase NO concentration and the C(O) concentration, giving an apparent order with NO of just over unity.

In the regime above 925 K, surface complexes become unstable in significant numbers, and the surface presents many opportunities for dissociative NO chemisorption. The temperature dependence of the rate begins to reflect the limitation imposed by the kinetics of the dissociative step itself (180 kJ/mol). Since the same “break point” between low and high temperature regimes is seen in the kinetics of NO attack on surfaces of widely differing reactivity (see Fig.1), it is not a change in the density of sites per unit surface area that is key in determining the existence of a break point. Rather, it is the sudden opening up of a particular type of site, in a narrow temperature window, that determines the break point. It is the steepness of the distribution of the activation energy distribution that makes it look as though there is one particular type of site involved\(^5\).

\subsection*{3.0 Reactivities of Carbons to Nitric Oxide}

As noted above carbons derived from different original materials are found to show similar behaviour, in terms of the trends, but there are significant differences in actual reaction rates, see Figures 1 through 3. Naturally, the reported rates of reaction could have been influenced by mass transfer, but virtually all workers whose data are shown claim chemical reaction itself was the rate determining step.

Accepting the claim that all of the rates were intrinsic reaction rates, our purpose was to
examine the reactivities of as large variety of carbons as possible using published data. The list of carbons represented in the figures is given in Table 1. The data in Figures 1 and 2 have been presented on a per unit surface area and per unit mass basis, respectively. Figure 3 extends the comparison of Figure 2 to a broader range of temperatures.

Not all workers provided carbon surface areas, which is why not all data sets are shown on all figures. The conversion of reaction rate data from one basis to another was performed using known surface areas, and design equations for packed bed reactors (except in the case of X. Chu and L.D. Schmidt56). As an example, using the data of Furusawa et al.39, they reported a rate constant \( k = 0.7 \text{ sec}^{-1} \) for char at 775 K, based upon a simple first order packed bed reactor model which can be represented as:

\[
\ln \left( \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right) = -k \cdot \theta
\]

where \( \theta \) is the residence time, sec. The conversion of this rate constant to our bases can be accomplished by

\[
k' \left( \frac{g_{\text{NO}}/g_{\text{C}}-\text{sec-atm}}{} \right) = k(\text{sec}^{-1}) M_{\text{NO}}/(\rho_{\text{C}} R T)
\]

where \( M_{\text{NO}} \) is the molecular weight of NO (30 g/mol), \( \rho_{\text{C}} \) is the bed density of the char (approximately 0.7 g/cm\(^3\)), \( R \) is the gas constant (82.06 cm\(^3\) atm/mol*K), and \( T \) is the temperature. Thus

\[
k' = (0.7 \text{sec}^{-1})(30 \text{ g/mol})/(0.7 \text{ g/cc})(82.06 \text{ cc-atm/mol-K}) (775K)
\]

\[
= 4.72 \times 10^{-4} \frac{g_{\text{NO}}}{g_{\text{C}}-\text{sec-atm}} = 1.7 \frac{g_{\text{NO}}}{g_{\text{C}}-\text{hr-atm}}
\]

X. Chu and L.D. Schmidt56 used scanning tunneling microscopy (STM) to study carbon/NO reaction kinetics. This technique has been recently developed to study gas-solid reactions. Basic idea is to measure the number and size of monolayer pits on the basal plane versus temperature and time. The constant size and linear growth rate of monolayer pits suggests that reaction initiates on point defects. The growth rate gives the gasification rate.

The rate or turnover frequency is given by:

\[
\left[ \frac{\text{atoms reacted}}{\text{edge atom} \cdot \text{sec}} \right] = \frac{\rho_{1120} \pi D dD/dt}{\rho_{1120} 2 \pi D H} = \frac{\rho_{1120} dD/dt}{\rho_{1120} 2 H} = 0.469 \frac{dD}{dt} = k_{0,NO} \exp \left[ -\frac{E}{R T} \right] \cdot P_{\text{NO}}
\]
where D is the diameter of the monolayer pit, Å; \( \rho_{1000} = 0.377 \) carbon atom/Å\(^2\) (on the basal plane), \( \rho_{1120} = 0.120 \) carbon atom/Å\(^2\) (on the step face); H is the monolayer step in basal plane, \( H = 3.35 \) Å for graphite.

To compare these rate data with those obtained by conventional methods, something has to be known about what fraction of carbon atoms are edge atoms. The average area per atom is 3.2 Å\(^2\), the weighted average of the area of edge and cleavage surface atoms. Taking 8.3 Å\(^2\) as the surface area of an edge atom, the surface per gram of edge atoms can be calculated from

\[
8.3 \times 10^{-20} \frac{m^2}{\text{atom}} \cdot 6.023 \times 10^{23} \frac{\text{atoms}}{\text{eq}} \cdot \frac{1}{12} \frac{\text{eq}}{g} = 4166 \frac{m^2}{g \text{ edge atoms}}
\]

A typical graphite, such as that used by Chan et al.\(^{32}\), has a surface area of 3.7 m\(^2\)/g. This would imply a fraction of surface atoms

\[
\frac{3.7 \frac{m^2}{g}}{4166 \frac{m^2}{g \text{ edge atoms}}} = 8.88 \times 10^{-4} \frac{\text{edge atom}}{\text{atom}}
\]

To put Chu and Schmidt's data on a comparable basis, this factor is applied to those data (not knowing, of course, if this was at all the case for their actual sample).

For the purpose of comparison, the units of the rate, \( r' \), has been converted to some conventional rate units, \( r \), by the following expression:

\[
r \left[ \frac{g}{m^2 \cdot \text{hr}} \right] = r' \left[ \frac{\text{atoms reacted}}{\text{edge atom} \cdot \text{sec}} \right] \cdot 3600 \frac{\text{sec}}{\text{hr}} \cdot \frac{1}{6.02 \times 10^{23}} \frac{\text{mol}}{\text{atoms}} \cdot 12 \frac{\text{g}}{\text{mole}} \cdot \frac{1}{3.2 \times 10^{-20} \frac{\text{atom}}{m^2}} \cdot 8.88 \times 10^{-4} \frac{\text{edge atom}}{\text{atom}}
\]

The above expression gives the rate in grams of carbon reacted. Naturally, there is a need to further convert this reactivity to a "grams of NO reacted" basis. The assumption was made that the reaction stoichiometry was 1 mol of NO reacted per mol of C reacted. Thus \( r \) needed to be further multiplied by a factor of 2.5 for comparison with the other data.
Figure 1 shows that there exist large differences in reactivity of different carbons. Disregarding the results for graphon, there is a spread of nearly two orders of magnitude in the rates. The reactivity of Taiheiyo coal char, for example, is about two orders of magnitude higher than a demineralized coal char or an activated carbon. The “break” in mechanism at around 900 K is clearly visible in several studies. A remarkable consistency is seen in the results given by very different materials, and there is no clear effect of starting material or purity. There is not an immediately apparent reason for why the graphon is so much at variance with the other results.

The curves in Fig. 2 show almost the same spread as the data plotted in Figure 1. The surface area basis of Figure 1 would normally be considered a more fundamental basis on which to compare results. This might suggest that the BET surface area is not necessarily a very effective characterization of the reactive surface area of the char. Why this should be is unclear. A number of studies\textsuperscript{55, 57, 58} have suggested that gasification reactions occur primarily outside of the microporous network on the surface of large pores and on the external surface of char. It is, however, difficult to draw such a conclusion based upon these results alone.

Figure 3 shows data on the same basis as does Figure 2, but covering a broader range of conditions. Yamashita et al.\textsuperscript{19} employed reaction conditions involving both pure NO as well as NO in the presence of O\textsubscript{2}. Generally, the pure NO results at higher temperatures extrapolate to the values Yamashita et al. obtained in pure NO. The NO destruction reaction in the presence of O\textsubscript{2} is clearly faster.

The results of Lai et al.\textsuperscript{17} are also not necessarily directly comparable to the others, because these were obtained on carbon which had been deposited on CaO. This system shows generally higher reactivity than the purer carbon systems, and also appears to operate with “high-temperature-regime” kinetics to much lower temperatures.

The reasons for the discrepancy between the results of Schuler et al.\textsuperscript{30,41} and the other data is not understood. These workers employed very low concentrations of NO (10 ppm), and observed apparently fractional order kinetics. It might be because of their unusual conditions, they
were in a different kinetic regime, and the representation of their data on the same basis as the others is therefore inappropriate.

4.0 Plans for the Upcoming Quarter

As the result of the completion of most of the TGA system, actual experimental testing can begin during next quarter. We have made some minor modifications to the TGA system which are due to the fact that the volume of the DuPont 951 TGA is ten times smaller than the TGA that we used before. Because of the large NO consumption we are forced to introduce the gas flow through the TGA. The full description of the TGA system will be given in next quarterly report.

We are looking forward to performing some comparative reactivity measurements for graphite, graphite fibers and coconut char in TGA.

5.0 References

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<td>High-Volatile Bituminous Coal Char</td>
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<td>Fixed Bed</td>
<td>673-1223</td>
<td>0.06-0.32</td>
<td>1173 K 1 hour</td>
<td>Rodriguez-Mirasol et al. (1993) 59</td>
</tr>
<tr>
<td>Blanzu Anthracite Coal Char</td>
<td>294</td>
<td>Fixed Bed</td>
<td>673-1223</td>
<td>0.06-0.32</td>
<td>1173 K 1 hour</td>
<td>Rodriguez-Mirasol et al. (1993) 59</td>
</tr>
<tr>
<td>Bituminous Coal Char</td>
<td>32.6</td>
<td>Fixed Bed</td>
<td>1073-1173</td>
<td>0.03-0.1</td>
<td>NA</td>
<td>Johnsson (1990) 60</td>
</tr>
<tr>
<td>Brown Coal Char</td>
<td>194.5</td>
<td>Fixed Bed</td>
<td>1073-1173</td>
<td>0.03-0.1</td>
<td>NA</td>
<td>Johnsson (1990) 60</td>
</tr>
<tr>
<td>Petroleum Coke</td>
<td>5.1</td>
<td>Fixed Bed</td>
<td>1073-1173</td>
<td>0.03-0.1</td>
<td>NA</td>
<td>Johnsson (1990) 60</td>
</tr>
<tr>
<td>Coke deposited over CaO</td>
<td>NA</td>
<td>Fixed Bed</td>
<td>673-972</td>
<td>0.179</td>
<td>NA</td>
<td>Lai et al. (1988) 17</td>
</tr>
<tr>
<td>Brown Coal Char</td>
<td>NA</td>
<td>Fixed Bed</td>
<td>573</td>
<td>2.03</td>
<td>873 K 1 hour</td>
<td>Yamashita et al. (1993) 19</td>
</tr>
<tr>
<td>Brown Coal Char + Cu</td>
<td>NA</td>
<td>Fixed Bed</td>
<td>573</td>
<td>2.03</td>
<td>873 K 1 hour</td>
<td>Yamashita et al. (1993) 19</td>
</tr>
<tr>
<td>Coal Char + KOH</td>
<td>1790</td>
<td>Fixed Bed</td>
<td>873</td>
<td>0.4</td>
<td>1173 K 5 minutes</td>
<td>Illan-Gomez et al. (1993) 18</td>
</tr>
<tr>
<td>Olive Stone Char</td>
<td>734</td>
<td>Fixed Bed</td>
<td>873</td>
<td>0.4</td>
<td>1173 K 5 minutes</td>
<td>Illan-Gomez et al. (1993) 18</td>
</tr>
<tr>
<td>Phenol-Formaldehyde Resin Char</td>
<td>723</td>
<td>Fixed Bed</td>
<td>873</td>
<td>0.4</td>
<td>1173 K 5 minutes</td>
<td>Illan-Gomez et al. (1993) 18</td>
</tr>
<tr>
<td>Almond Shell Char</td>
<td>457</td>
<td>Fixed Bed</td>
<td>873</td>
<td>0.4</td>
<td>1173 K 5 minutes</td>
<td>Illan-Gomez et al. (1993) 18</td>
</tr>
<tr>
<td>Carbon Fiber</td>
<td>507</td>
<td>Fixed Bed</td>
<td>873</td>
<td>0.4</td>
<td>1173 K 5 minutes</td>
<td>Illan-Gomez et al. (1993) 18</td>
</tr>
</tbody>
</table>

Table 1. Previous Studies of the NO/C Reaction
Figure 1. NO-carbon reaction rate constant expressed on a surface area basis.
Figure 2. NO-carbon reaction rate, per unit mass of carbon reactant.
Figure 3. NO-carbon reaction rate constant, as in Figure 2, but including data obtained at lower temperatures and in the presence of oxygen.