

AN EXAMINATION OF THE TWO KINETIC REGIMES OF THE NITRIC OXIDE-CARBON GASIFICATION REACTION

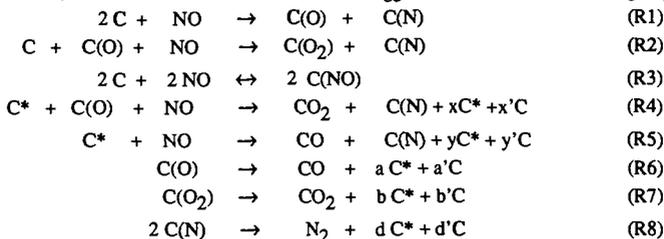
E.M. Suuberg, H. Teng, and I. Aarna
Division of Engineering, Brown University,
Providence, RI 02912

Keywords: Nitric Oxide, Carbon, Gasification

INTRODUCTION

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 (< 473K) [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 CO₂ via (R4). The reaction (R2) allows for some small amounts of stable CO₂-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 Oriksa 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 1, which will be discussed below.

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.

Results and Discussion

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 1. 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 1. 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 2. 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 1 - 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 1, 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].

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 3, 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. 3, 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 also represented in Figure 3, 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 1).

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 paper.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support provided by the USDOE under grant DE-FG22-94PC94218.

REFERENCES

1. Suuberg, E.; Teng H.; Calo, J. *23rd Symp. (Int.) on Combustion*, The Comb. Inst., Pittsburgh, 1990; p 1199.
2. Teng, H.; Suuberg, E.M.; Calo, J.M. *Energy and Fuels*, 1992, 6, 398.
3. Aama, I.; Suuberg, E.M., paper presented at this meeting.
4. Teng, H.; Suuberg, E.M. *J. Phys. Chem.*, 1993, 97, 478.
5. Orikasa, H.; Suzuki, T.; Kyotani, T.; Tomita, A.; Martin, R., *Proc. Carbon '95*, p 626, American Carbon Society, 1995.
6. Yamashita, H.; Tomita, A.; Yamada, H.; Kyotani, T.; Radovic, L.R., *Energy Fuels*, 1993, 7, 85.
7. Suzuki, T.; Kyotani, T.; Tomita, A., *I&EC Res.*, 1994, 33, 2840.
8. Vorres, K. *Energy and Fuels*, 1990, 4, 420.
9. Suuberg, E.M. in *Fundamental Issues in Control of Carbon Gasification Reactivity* (J. Lahaye and P. Ehrburger, Eds.), p. 269, Kluwer, Boston, 1991.
10. Tian, Y., Doctoral Dissertation, Chemistry, University of Essen, Germany, 1993.

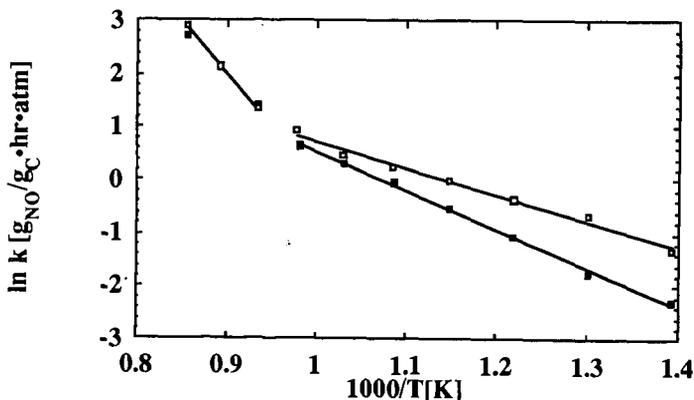


Figure 1. A comparison of the rate constant for NO reduction by resin char with cleaned surface (open squares) and uncleaned surface (closed squares). The NO pressure was 2 kPa.

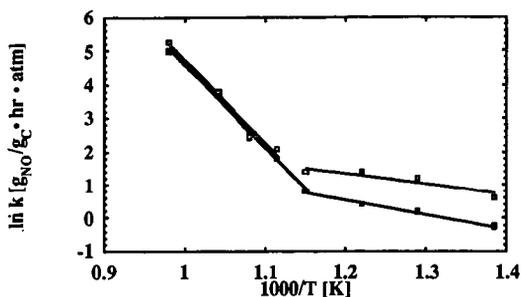


Figure 2. The effect of heat treatment upon the reactivity of Wyodak char. The open points are for a sample heated to 1273 K at 30 K/min, and the closed points are for a sample heated for four hours at 1273 K (see text). The NO partial pressure was 10 Pa.

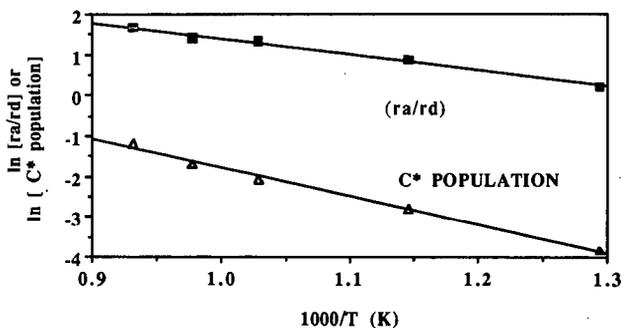


Figure 3. The variation of relative rates of rapid turnover and desorption processes with temperature, and the variation of rapid turnover site population with temperature. Values obtained from TGA experiments at 1 to 10 kPa NO pressure.

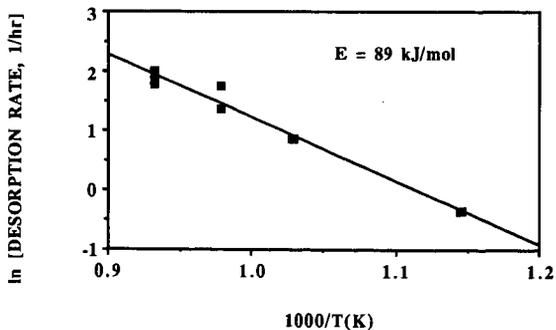


Figure 4. Oxide desorption rate, after removal of NO from the TGA.