NO_x - Char Reactions: Kinetics and Transport Aspects

**J. M. Calo and E. M. Suuberg (Principal Investigators)
H. Teng and I. D. Milosavljevic**

**Chemical Engineering Program
Division of Engineering
BROWN UNIVERSITY
Providence, Rhode Island 02912**

**Quarterly Technical Progress Report
April 1, 1990 - June 30, 1990**

Received by OSTI
NOV 13 1990

**Prepared for:
U. S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236**

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1.0 Project Summary

The principal goal of this project is to develop a mechanistic understanding of the processes by which carbons reduce NO to N₂. The reaction of interest may be represented by the non-stoichiometric equation:

The relative yields of CO and CO₂ depend upon the reaction conditions, as will be described below.

The carbon selected for study in this program was a char derived from phenol-formaldehyde resin. This material has been noted to be a reasonable model for coal chars in most respects, except that its gasification behavior is not complicated by catalytic processes due to minerals. For a fundamental study such as this, the absence of catalytic effects is important. In addition to its being a reasonable model for coal chars, the phenol-formaldehyde resin chars also have the advantage that they have been extensively studied with respect to gasification in oxygen and CO₂.

In the first phases of the project, the global kinetics of the process were established. In more recent work, attention has been turned to the individual steps in the mechanism. Recent quarterly reports have detailed the role of both chemisorption and desorption processes in determining the course and kinetics of the process. This report continues the reporting of results obtained along these lines, and draws an important new conclusion concerning the number of separate processes involved in determining the kinetics.

2.0 Project Objectives

These have been extensively summarized in previous quarterly reports. Briefly, the present project is motivated by the need to reduce NO_x emissions from combustors, especially coal combustors. Since NO_x species derive from both the fuel and from the combustion air, it is impossible to completely prevent the formation of NO_x, although certain fuel-air mixing strategies have proven effective at reducing emissions in many cases.

Still, there remains a need to develop alternative strategies for NO_x reduction. Reactions with carbon are known to be effective at reducing NO to N₂, and remain interesting candidates in a wide variety of possible applications. These reactions are known to be important in reducing NO_x emissions from fluidized bed coal combustors, in which the coal char itself serves as the reducing agent. It has also been hypothesized that the reactions of NO in the pores of burning coal particles might serve to reduce emissions to levels below which

they might otherwise be. Equally important to the objective of reducing NO emissions (NO being the chief component of NO_x) might be the development of downstream scrubbing devices based on the effective use of carbon. These have already been explored to a certain extent, in that carbon has been used as a catalyst for a scrubbing process that involves the reduction of NO by ammonia, it has been studied for use in a packed bed scrubber with no other added reactants, and it has also been used as a support for automotive "three-way" catalysts. Consequently, the choice to study a char which may be viewed as a model for coal should not be viewed as precluding the possible use of carbon in these other ways.

The present project is intended to fill a need for a better mechanistic understanding of the reaction of NO with carbon. The hope is that such a better understanding might facilitate development of new strategies for the use of carbon in reducing NO.

3.0 Background

The mechanisms of oxidation of char in O₂, CO₂, and H₂O are not yet well understood in many respects¹⁻⁹. The reactions of carbons with NO are even less well characterized. The reactions have been hypothesized to include¹⁰:

The last reaction is a carbon surface catalyzed oxidation of CO by NO, based upon the observation that reduction of NO by char is enhanced by the presence of CO^{11,12}. A reaction of this type is also noted on iron oxide¹³ and quartz¹⁴. In carbons, the reaction might involve impurities in the carbons and may be unimportant below 720K¹⁵, except in alkali catalyzed systems¹⁶. The reaction of NO with carbon is generally reported to be first order with respect to NO^{12,15,17,18}, in contrast to reactions of carbons with O₂, which have a fractional order¹⁹. The ratio of CO to CO₂ in the products of gasification of carbons by NO increases with temperature^{12,17,18,20,21}. The shift in product ratio is accompanied by a change in mechanism at a temperature in the neighborhood of 873 to 953K^{12,17,22}. In a high enough range of temperatures (1273-1773K), the products of reaction are essentially pure CO and N₂ in the expected ratio of 2:1³³.

The role of O₂ in the NO-char reaction has been studied to a limited extent^{30,31}. The oxygen was seen to accelerate the rate of reduction at temperatures below about 680°C³⁰. In another study, the possibility of conversion of NO to NO₂ was noted³¹.

One proposed mechanism for the reaction of carbon with NO is as follows¹²:

This reaction scheme was used to derive a Langmuir-Hinshelwood type rate expression for the stationary state rate of NO consumption¹²:

$$-r_{\text{NO}} = \frac{k_1 P_{\text{NO}} (k_2 P_{\text{CO}} + k_3)}{k_1 P_{\text{NO}} + k_2 P_{\text{CO}} + k_3} \quad (1)$$

The authors of this model noted its shortcoming in terms of failing to correctly predict an overall first order rate with respect to NO pressure. An alternative mechanism is somewhat more elaborate¹⁸:

The original presentation of this model contained two reversible steps of form R5, representing the formation of the two different types of $\text{C}(\text{O} \cdot \text{ON})\text{C}$ complexes that react according to R6 and R7.

There is general agreement that the first step is chemisorption of NO at almost any temperature of relevance. It probably involves addition of NO in an N-down configuration²³. The reversible physisorption of NO appears to dominate below about 90K³⁴, but above 120K the process begins to become somewhat irreversible^{18,24}. The sorption of NO on freshly cleaved carbon surfaces has been noted to be irreversible at room temperature^{23,32}, with an initial adsorption heat of 222 kJ/mol²³. It was also concluded that the basal planes of graphite are relatively unreactive to NO, at temperatures up to 673K³⁵.

One study has suggested that a significant amount of undissociated, but chemisorbed, NO might exist on the surface to temperatures up to at least 373K²⁵, and another seems to suggest that all NO is lost by 423K³². The conversion of surface-bound NO to carbon oxide products is observed at temperatures at least as low as 298K³⁶. The evidence thus favors an irreversible chemisorption of NO, followed by release of N_2 and formation of carbon oxide surface complexes, as suggested in R4 (or R1). Other oxides of nitrogen are rarely formed in significant quantities in such systems, though some traces of N_2O may be observed at low temperatures (<650K)²¹. Formation of N_2 involves either the combination of dissociated N atoms on the surface¹¹, or the N-N bond forms simultaneously with dissociation of one or both N-O bonds. Since there is no evidence of cyanogen in such

reaction systems^{12,15,37}, it has been suggested that dissociated, chemisorbed N is unlikely to play a significant role¹⁵. This conclusion appears, however, to be at odds with the observation that N₂ is an important high temperature desorption product^{36,38}.

The overall conversion of NO to N₂ appears to depend upon the chemical structure of the carbon; the more highly heat treated a carbon, the lower the thermal stability of NO on its surface, but the higher the efficiency in converting NO to N₂²⁵. There however appear to be different effects of thermal treatment on the reactivity of the carbon towards NO in different temperature ranges³⁹.

The route for formation of CO is different in the above two mechanisms. In the sequence R1-R3, CO comes from thermal desorption of carbon oxide groups. In the sequence R4-R8, the CO comes from a direct attack of NO on surface oxides. The route for formation of CO₂ is likewise different in the two mechanisms. The sequence R1-R3 involves an attack of CO on surface oxides, whereas R4-R8 involves NO attack on surface oxides. Neither allows for the desorption of oxides as CO₂. The authors of both of the above mechanisms acknowledge the possible surface catalyzed reaction of CO with NO (R8).

The possible role of mass transfer in affecting the results of the above cited studies cannot be overlooked. A recent study has suggested that an effectiveness factor near unity is possible at around 900K, but may fall to about 0.2 for a 100µm particle at 1200K²⁶.

The global NO carbon gasification rate expression is:

$$dm_c/dt = A_g \exp(-E_g/RT) P_{NO}^n \quad (2)$$

where m_c is the mass of carbon and n the reaction order with respect to NO. The high temperature regime is characterized by an activation energy of 180kJ/mol, whereas the low temperature regime shows no unique value of activation energy³⁸. Below a temperature of about 923K (650°C), the low temperature process involves an activation energy that rises from about 63kJ/mol to 88kJ/mol with increasing temperature.

The values of activation energy obtained at low temperatures are in general agreement with many others in the literature^{15-18,20,21,27}, although in a few cases the low values were reported to apply to temperatures even over 1000K^{20,27} (see Table I). The change from low to high activation energy with increasing temperature has been noted previously by two groups^{12,17}. The NO partial pressure range of the present work is higher than the ranges of the earlier studies that yielded similar non-constant activation energy behavior.

Our earlier results indicated that the low temperature regime is probably characterized by a dominance of the process of oxide desorption from the surface, in line with the reaction sequence (R1) + (R3). The activation energy distribution derived from desorption measurements of CO, CO₂, and N₂ are consistent with a low temperature regime

whose temperature dependence is determined mainly by the desorption of chemisorbed oxygen and nitrogen species. This leads to two questions- why is the low temperature regime then first order in NO partial pressure and are the product ratios obtained in desorption experiments consistent with the steady gasification experiment product ratios? These questions will be addressed in this report.

4.0 Experimental

A thermogravimetric device (TGA) was used for the present study. The system and general approach have been described previously (see earlier quarterly reports and refs. 19 and 38). The chars selected for study were the same chars as used in the earlier study. These chars are derived from phenol-formaldehyde resins, synthesized in-house to keep the level of potentially catalytic impurities as low as possible. Pyrolysis involved heating in helium for two hours at 573K, and then two hours at 1273K. The resulting char was a glassy carbon with an H/C atomic ratio of approximately 0.1 and an O/C ratio of approximately 0.01. The experiments described here were run so that surface area did not change significantly during the course of the experiment. The results reported here were all obtained on samples that had been burned off to an extent greater than a few percent, and the presumption is that the micropore area (about 100-200 m²/g) is fully accessible to NO.

5.0 Results and Discussion

Figure 1 displays the variation of activation energy and product ratio reported earlier, showing the change in controlling mechanism at a temperature of about 923K. Higher CO/CO₂ ratios are obtained at higher temperatures, in agreement with the literature^{12,17,18,20,21}. In what has been here arbitrarily defined as the low temperature regime (<923K), the variation in CO/CO₂ ratio with temperature shown in Fig.1 implies an activation energy for formation of CO that is approximately 20kJ/mol higher than that for formation of CO₂. In the high temperature regime (>923K), the CO/CO₂ ratio does not vary much with temperature. The range of temperatures examined is relatively modest (only up to 1073K), so the variation in product ratio may not be significant partly for this reason. It should be noted that literature reports of significant variation of the ratio at high temperatures^{11,17,21} have normally come from packed bed experiments in which secondary reactions of primary CO₂ with the char could possibly affect the reported ratios.

The global order of reaction with respect to NO (the parameter *n* in eq. 2) was determined in experiments in which the NO partial pressure was varied between 1.0 and 10.1

kPa. The process of gasification in both temperature regimes is approximately first order with respect to NO (and not fractional at high temperatures, as we earlier believed²²).

Earlier observations²² of transient behavior during changes in NO pressure led to a suspicion that there was a significant variation in surface oxide inventory with such changes. Experiments were conducted in which the surface was allowed to build up oxides to a steady value, followed by immediate desorption in inert gas. The key quantities obtained from such an experiment include the steady rate of gasification in the presence of NO (r), the rate of desorption immediately following the removal of NO (r_d), the total amount of mass that could be isothermally desorbed in a ten hour period following the removal of the NO (m_d), and the total inventory of desorbables on the surface (m_0), as revealed by a two hour desorption of all oxides at 1223K. The quantity m_0 includes the species that constitute m_d . The rate of desorption r_d as a function of time and temperature was used to obtain the activation energy distribution for desorption.

The products of desorption are shown as a function of temperature in Fig. 2. The main product is clearly CO, but N_2 and CO_2 are present in significant amounts. N_2O was not measurable in these experiments, nor was NO. These results suggest that the reaction R1 (or R4) cannot really represent the chemisorption step, since there must be long-lived nitrogen containing species on the surface, capable of releasing N_2 at long times in the absence of NO. This indirectly supports the existence of C(N) complexes, which would be expected to provide a source of N_2 at high temperatures. The C(NO) complexes themselves are thought to be unstable at high temperatures, though firm proof for this is not yet available.

The ratio of the measured desorption rate at the instant the NO was cut off (r_{d0}), to the steady gasification rate immediately prior to cutoff of the NO (r) was 1.44 at 873K, 0.89 at 973K, and 0.71 at 1073K (all at $P_{NO} = 4.1\text{kPa}$). It was necessary to extrapolate the actual desorption curves back to the instant of NO cutoff to estimate r_{d0} and the uncertainty in the ratios is about ± 0.1 . Since CO dominates the desorption products, these results immediately show that the reaction R3, involving desorption of CO, is fast enough that it can be a significant contributor to the overall gasification rate, especially in the low temperature regime. The fact that the r_{d0}/r is greater than unity is reasonable, because r_{d0} includes the loss of oxygen and nitrogen, whereas r does not (they are replenished on the surface at steady state gasification conditions). If expressed on a carbon mass loss basis, the value of r_{d0}/r at 873K is only 0.45, showing a significant contribution of other processes (calculated from the data of Fig. 2 and the mass ratio above). The ratio of the rate of formation of CO by desorption compared to that from steady gasification is calculated to be 0.87. Thus most CO is formed by direct desorption, but there is a separate path to CO_2 that

is not reflected in the desorption process. This will be discussed below.

The desorption results directly contradict the conclusion of other workers that the carbon-oxygen complexes disappear at temperatures around 950K¹⁷. In fact, TPD experiments show some complexes to be quite stable to much higher temperatures⁴⁰.

The rate of desorption r_d of course depends upon the number of oxides plus nitrogen remaining on the surface. It was noted to be essentially first order in the amount of desorbable species, for a significant time after cutoff of the NO. The first order rate constants that could be calculated from these data give an apparent activation energy for desorption of the least stable species (those that desorb earliest) of about 88 kJ/mol following gasification experiments at 4.1 kPa NO. Similar desorption experiments following gasification under 10.1 kPa NO gave an activation energy of 79 kJ/mol. These activation energies reflect the apparent activation energy for the desorption of CO, mainly. They are quite similar to the activation energy for the high temperature end of the low temperature regime of steady gasification. This must at least in part be due to the fact that CO rapidly becomes more important as a product at these temperatures (around 873K), and the change in gasification rate with temperature reflects its increasingly significant role in the mix of products.

The mass that could be desorbed at any temperature (m_d) was determined by measuring the total mass loss from the sample during a 10 hour period following NO removal (after steady state gasification). This time was sufficiently long such that the rate of desorption, determined in the TGA, became so small as to be difficult to accurately measure. The pressure dependence of m_d can be represented by $m_d \sim P_{NO}^n$, where $n=0.25$ at 973K and 0.21 at 1073K.

The total inventory of desorbables on the surface (m_0) was determined by raising the temperature of the sample to 1223K. This is an arbitrarily chosen temperature, used by many workers to "clean" the majority of oxides off of a carbon surface. The total mass loss of the sample, from the time that the NO was removed to the time that the rate of desorption of oxides dropped to essentially unmeasurable levels at 1223K, is what is reported as m_0 . The quantity m_0 is crudely proportional to the 0.16 power of NO concentration at 973K and to the 0.08 power at 1073K. Thus the NO pressure dependence of m_d is somewhat greater than the NO pressure dependence of m_0 .

The quantity m_0 is not a strong function of temperature. Its value was 5.7×10^{-2} ($\pm 0.7 \times 10^{-2}$) mg/m², regardless of the temperature at which the char was previously gasified (between 873K and 1073K). The quantity m_d is a function of temperature, with $d[\ln(m_d)]/d(1/T) \cong -7200K$. This must reflect the distribution of activation energies for desorbing surface species--as the temperature is raised, the fraction of species that can be

desorbed from the surface in the time available, increases. This temperature dependence is not exhibited by m_0 , because the temperature is high enough in the experiments used to determine m_0 that the majority of **surface species** are removed from the surface, regardless of their desorption activation energies. This hypothesis is supported by examination of the TPD spectrum of the char surface⁴⁰.

It has already been concluded that the rate of desorption of CO is high enough that the reaction (R3) can make a significant contribution to the overall rate of gasification. The importance of CO₂ as a product of the reaction in the low temperature regime seems to require that a separate route be available for forming this product. The route must apparently involve closely coupled attack of NO on the surface and CO₂ release, since it ceases to be important when NO is removed. This leaves open the possibility of reactions of the type R6 or R7 during steady gasification in the low temperature regime. In light of the results reported in the previous quarterly, it would be expected that the inventory of NO containing complexes on the surface would depend upon temperature and pressure. This would make it difficult to reconcile the approximately first order nature of the gasification process in terms of R6 and R7, unless the pressure dependence of the overall complex inventory were small, and the rate of formation of the complexes was fast compared to R6 and/or R7. At present, this cannot be ruled out.

Alternatively, the processes might involve the following:

In this case, the process might be more easily reconciled with its apparently first order dependence upon NO, since any oxide on the surface would be capable of reacting according to R9. Another possibility is that attack of NO on the surface might form oxide complexes that are so unstable that they desorb immediately upon formation under steady gasification conditions. These unstable complexes would have to include all that form CO₂. This is not implausible, but the mechanism would have to be challenged on the basis that the stoichiometric requirements would seem to force the reaction rate to be something closer to second order in NO, since CO₂ is a major product..

The different possibilities for formation of CO₂ were explored in experiments in which a char was initially gasified at a fixed temperature in NO, to give a surface representative of that in steady gasification. Then the char was cooled, still in NO, over the course of three hours, to 323K, and left in NO for varying lengths of time (1 hour to 24 hours). The presumption was that this might result in "filling in" reactive surface sites that form CO₂-releasing complexes that are **unstable at** the gasification temperature. The char was then isothermally evacuated at 323K, to constant mass, to remove physisorbed NO. The surface species that were formed during the preceding cooling cycle were then desorbed by

heating back to the original gasification temperature at a rate of 22.5K/min, in helium. The products that were obtained by this procedure were N_2 , NO, CO_2 , N_2O , and CO. The results are shown in Table II, in terms of the ratio of CO_2 to CO. These data are for the case in which the time of exposure of the char to NO was brief-- the char was permitted to soak in NO at low temperatures for only 1 hour. Soaking in NO at low temperatures for longer times always gave higher ratios of CO_2/CO , suggesting that the process of formation of CO_2 complexes is kinetically limited.

The ratios of CO_2/CO obtained in the experiments of Table II were compared to the ratio of CO_2/CO that could be calculated from the steady state gasification product composition data (such as that in Fig. 1), by subtracting the contribution that desorption makes to the total. The molar rate of carbon loss by desorption relative to the loss by steady gasification is shown in Fig. 3. The composition of the desorbing species is seen in Fig. 2. The calculation of the ratio that would be expected from the experiments that promote formation of the unstable complexes can be performed as follows; the ratio r_{dO}/r provides an estimate of r_a/r , from $1-r_{dO}/r = r_a/r$, where r_a is the rate of formation of product from the direct attack of NO giving unstable complexes. Since the same calculation can be performed for both CO and CO_2 individually, the ratio r_{aCO_2}/r_{aCO} may be calculated. This ratio would be expected to equal the experimental composition ratio for the desorption of the unstable complexes only if no other product formation processes contribute. This is seen to be the case in Table II.

The implication of the agreement between the calculated and measured CO_2/CO ratios of Table II is significant. It means that there is no need to account for any other processes of product formation, apart from the slow desorption (of mainly CO) and the direct attack of NO to give unstable complexes. The change in the mechanism that appears to occur at around 923K really reflects the transition from a process which is dominated by the simple desorption of surface oxides at low temperatures, to a process that is dominated by the formation of unstable oxides by direct attack of NO at high temperatures. The competing processes do contribute significantly to the overall rates even in the temperature regime in which they are not dominant. There is not a clean change in mechanism, but rather a gradual transition at around 923K.

The presence of NO and N_2O has not been noted in any of the higher temperature isothermal desorption experiments, so the corresponding surface species are probably unstable under those conditions. They are seen in the experiments used to search for unstable complexes because of the particular manner in which these experiments were performed (they can both form and desorb at low temperatures). This is of little relevance

under steady gasification conditions, except that N_2O is a trace product at low temperatures.

7.0 Plans for the Upcoming Quarter

Work in the next quarters will be devoted to resolving a central question raised by the work reported here. This is the question concerning the mechanism of NO interaction with the surface, yielding unstable complexes. As was noted above, this could involve the mechanism of Smith et al., via reaction R6 or R7, or a variant of these that may be represented as:

and

Alternatively, or reaction R9 accompanied by the following might be the principal step:

The work will focus on the establishing the existence of $C(NO)$ complexes on the surface as key intermediates. In their absence, the R9-type sequence will be the choice by default.

Work will also continue on clarifying the mechanism of chemisorption of NO, an issue that is obviously interrelated with the above.

6.0 Conclusions

The present study suggests an important role for oxide desorption processes in NO gasification of chars. In the low temperature regime, CO formation is essentially desorption controlled. The mechanism of release of CO_2 is now established to involve the production of unstable complexes by attack of NO on the surface.

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Table I- Activation Energies for the NO-Carbon Reaction

<u>Carbon</u>	<u>Surface Area^a</u>	<u>Reactor</u>	<u>Temp. Range (K)</u>	<u>P_{NO}(kPa)</u>	<u>E (kJ/mol)</u>	<u>Ref.</u>
Sugar Charcoal	NA	Fixed Bed	578 - 723	0.19-2.9	34.3-54.8 42.3 ^b	15
Activated Carbon	0-1400	Packed Bed	648 - 978	0.16-0.68	approx. 80	21
Sugar Charcoal	1060	Packed Bed	723 - 873	<1.1	62.8 ^c , 75.7 ^d	18
Graphon	87	Packed Bed	1027 -1233	0.27-0.75	86.6	20
Coal Char 27	NA	Fluidized Bed	900 -1200	~0.04-0.08		67
Coal Char	175	Flow Reactor	1250-1750	0.05-0.65	137	28,29
Coal Char	20.3	Flow Reactor, Packed Bed	800 -1750	~0.05-1.0	145	11
Coal Char	17-20	Packed Bed	773 - 1118	0.03- 0.20	68.2 ^e , 245 ^f	17
Activated Carbon	800-1200	"	"	"	65.1 ^g , 177 ^h	
Coal Char	402	Packed Bed	723 - 1173	0.05-1.0	183 ⁱ	12
Deashed Coal Char	416	"	823 - 1123	0.20	223 ⁱ	
Graphite	3.7	"	873 - 1173	0.04-0.90 ^l	239 ⁱ	
Activated Carbon ^k	NA	Packed Bed	470 - 900	0.15	70	16
Coal Char	NA	Packed Bed	673 - 1023	0.002-0.04	120	26
Phenolic Resin Char	2-440	TGA	770 - 1073	1.0-10.1	180 ^l 63-88 ^m	this study

a - square meters/gram, various techniques (e.g. BET, CO₂- Dubinin)

b - Copper catalyzed

- c - oxidized surface
- d - H₂ treated surface
- e - below 953K
- f - above 953K
- g - mean value, two samples, below 953K
- h - mean value, two samples, above 953K
- i - value for temperatures above 873K, E is lower for lower temperatures
- j - feed contains CO
- k - K₂CO₃ impregnated
- l - above 923K
- m - below 923K

Table II- Product Ratios from Reactions of Unstable Sites

<u>CO₂/CO Molar Ratio</u>	<u>773K</u>	<u>873K</u>	<u>973K</u>	<u>1023K</u>	<u>1073K</u>
Experimental	2.39	1.38	0.74	0.53	0.42
Calculated	2.63	1.32	0.65	0.53	0.42

Figure 1. Temperature dependence of the rate of reaction of NO with phenol-formaldehyde resin char. The top panel illustrates the variation of activation energy for the reaction, and the lower panel illustrates the product ratio obtained at 4.1kPa. The reaction rate is given in grams of carbon lost per gram of char. All points are for chars with approximately the same surface area.

Figure 2. The yields of products of desorption from phenol-formaldehyde chars, gasified at the indicated temperatures, and then immediately subjected to desorption in inert gas at the same temperature.

Figure 3. The rate of desorption following NO cutoff to the rate of gasification immediately prior to cutoff (r_{d0}/r). All data from experiments in which the NO partial pressure was 76 torr.

END

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