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

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QUARTERLY TECHNICAL PROGRESS REPORT  
1 AUGUST, 1996 - 31 OCTOBER, 1996

PREPARED FOR:  
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<th>Report Type:</th>
<th>QUARTERLY</th>
<th>Reporting Period Start Date: 07/01/1996</th>
<th>End Date: 09/30/1996</th>
</tr>
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<td>Report Issue Date:</td>
<td>12/01/1996</td>
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<td>DOE Award No.:</td>
<td>DE- FG22 -94PC94218</td>
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1. 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 NO2 (since it is mainly a secondary product of combustion, e.g. see ref. 1), in recent years the emissions of N2O have also captured considerable attention2-8, 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 N2O problem. This is in part because earlier estimates of the importance of N2O in combustion processes were clouded by artifacts in sampling which have now been resolved9. This project is concerned with the mechanism of reduction of both NO and N2O 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 combustion10. This has been recently supplemented by the knowledge that heterogeneous reaction with carbon can also play an important role in reducing emissions of N2O2,6,7, but that the NO-carbon reactions might also contribute to formation of N2O2,8. The precise role of carbon in N2O 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 N2O formation and reduction still has to be improved"8. The same can be said of the NO-carbon system.

Also of importance in the context of "practical" application of the reported NO-carbon reaction kinetics is how other gases, particularly CO, CO2, O2 and H2O might affect these kinetics. There have been only few systematic studies concerning these effects.

Interest in the NO- and N2O-char reactions has been significant in connection with both combustor modeling, as well as in design of post-combustion NOx control strategies. As in the case of the NO-char reactions, the reaction of N2O with char is probably too slow
to be of significance in dilute particle phase, short residence time, pulverized coal combustion environments. 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. 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. Of course, it is also the lower temperatures of fluidized bed systems that lead to release of greater amounts of N\textsubscript{2}O from these systems, since the N\textsubscript{2}O destruction processes have higher activation energies than do formation processes. 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\textsubscript{X} emissions. The possibility of using carbons in the role of catalysts for the catalytic DeNO\textsubscript{X}-type processes has been explored. Their possible roles as catalyst supports has also been examined. The use of activated carbons for NO removal has been studied. 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. 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.

2. Experimental

During this quarter, the primary focus of activity continued to be the effects of other non-inert gases on the rates of NO reduction by carbon. Earlier, we had explored the effect
of CO and CO$_2$ on this reaction, and found that carbon monoxide enhanced the rate whereas carbon dioxide inhibited the rate. The same general experimental strategy was employed here to look at the effects of O$_2$ on the kinetics of the NO-carbon reaction.

A quartz packed bed reactor tube of 4 mm internal diameter and 500 mm overall length was used. Usually, a bed of 20-200 mg (in a predetermined length of 1-30 mm) of char particles, held in place with quartz wool, was located at the center of the tube. In the experiments with fly-ash, 250 mg of fly-ash was mixed with quartz wool to minimize the pressure drop in the reactor. The reactor was heated by an electrical tube furnace and a chromel-alumel thermocouple was placed inside the reactor tube for temperature measurements.

To test the importance of NO reduction by the quartz reactor tube and the quartz wool, blank runs were conducted by passing NO mixtures over the bed materials at different temperatures. The results showed no significant NO reduction (<1%, invariant with temperature). The same was not true when ordinary glass wool was used in the reactor. In this case, a few percent NO reduction was observed.

The reactor was outgassed prior to each run by a one hour vacuum pumping at room temperature. This was followed by thermal surface cleaning (at 1000°C for 1-2 hours in He) to remove surface oxides. Nitric oxide/helium mixtures of the desired concentration levels were prepared using a KIN-TEK precision calibration system. The desired NO/He or NO/O$_2$/He mixtures (10-300 ppm of NO in He or He/O$_2$) were obtained by controlling the flow rate of helium (usually 100 ml/min or 24 ml/min in the case of fly-ash) or He/O$_2$, and both the absolute temperature of the permeation membrane and the NO partial pressure in the KIN-TEK calibration system. In experiments in which the effect of O$_2$ concentration was explored, the desired O$_2$ concentration (0.5-5% of O$_2$ in NO/He mixture) was obtained by controlling the flow rate of O$_2$. 

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During the reactivity measurements, the product gases were continuously analyzed for NO and NO\textsubscript{2} using a chemiluminescence analyzer. In the presence of oxygen we expect the side reaction, Equation 1, to play an important role

$$\text{NO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{NO}_2$$  \hspace{1cm} (1)

It was found that in the reactor inlet only 1-5% of NO\textsubscript{X} corresponds to NO\textsubscript{2}, but at the reactor outlet no NO\textsubscript{2} was detected. This means that the reduction of NO\textsubscript{2} by carbon is much faster in comparison to NO, which is in agreement with other workers\textsuperscript{23}. In this work the reduction of NO was interpreted as a reduction of NO\textsubscript{X}. The other product gases, such as CO\textsubscript{2} and CO, can be analyzed by FTIR, but this was done only during the O\textsubscript{2} gasification experiments.

An Online Instruments TG-plus thermogravimetric analyzer was used for the O\textsubscript{2} gasification studies. The temperature and sample mass were recorded as a function of time. Products formed during the gasification experiments can be analyzed using the attached FTIR spectrometer, fitted with a multipass gas cell. Samples of 20-40 mg were dispersed on a circular platinum pan with a large, flat surface and raised sides, resulting in thin particle beds. The sample bucket was located in the heated zone of the TGA furnace, and a K-type thermocouple was placed about 5mm from the sample.

The gasification reactions were performed in a flow of O\textsubscript{2}/He mixture, with a purge gas flow rate of 140 mL/min. The reactant gas mixture contained 2% O\textsubscript{2} in He. Isothermal reaction at different temperatures was carried out for resin char and graphite. The samples were first surface cleaned at 950°C for 1 hour in helium to remove surface oxides. This was followed by a series of isothermal O\textsubscript{2} gasification experiments at different temperatures.

Specific surface areas of char samples were determined by the N\textsubscript{2} BET method at -196°C. A standard flow-type adsorption device (Quantasorb) was used for the measurements. Prior to surface area analysis, all samples were outgassed in a flow of nitrogen at 300°C for 3 hours.
The carbonaceous solids studied were resin char, graphite, fly-ash and Wyodak coal char. The resin char samples (180-290μm particle size) were derived from phenol-formaldehyde resins made in-house. The coal char (150-212μm) was also prepared in-house from the Wyodak sample of the Argonne Premium Coal Sample Program. The chars were prepared by a two hour pyrolysis, in inert gas, at a temperature of approximately 1000°C. The graphite (180-290μm) was prepared from graphite rods. The fly-ash samples are from the pulverized coal fired boilers of New England Power's Brayton Point Power Station. The flyash samples contained about 3.7 weight% of carbon. This sample was obtained under post low NOx burner retrofit combustion conditions. None of these samples was treated any further, except for surface cleaning (fly-ash samples were not even surface cleaned).

3. Results and discussion

During the last year or so, the main focus was on NO reduction by different carbonaceous materials (such as graphite, resin char and Wyodak coal char); however, the effect of coexisting gases such as CO, CO₂, O₂ and H₂O is not yet fully established. The presence of other gases significantly modifies the reaction kinetics. Generally, O₂¹⁹,²³ and CO²⁴-²⁶ appear to enhance the rate of reduction of NO, whereas the reaction have been reported to be inhibited by water vapor²⁴, at least in high temperature regime. In the last quarterly report we showed that the presence of CO₂ inhibited the NO reduction by graphite. We reported that the CO₂ inhibition effect could be masked by CO production in the case of resin char and Wyodak coal char. During this quarter, the effect of O₂ on reduction of NO was investigated. It was found that the reduction of NO was significantly enhanced in the presence of oxygen.

The presence of oxygen has been demonstrated many times to have a significant effect on the rate of NO reduction by carbons¹⁹,²³. Yamashita et al.¹⁹ concluded that the enhancement effect of oxygen results from the creation of additional active sites, during
oxygen attack on the carbon surface. They also showed that the oxygen effect was greatly enhanced by the addition of copper catalyst. Suzuki et al.\textsuperscript{23} proposed the following simplified reaction mechanism, where the rate enhancement is mainly due to the increase in the number of oxygen surface complexes, Equation 2:

\begin{align}
O_2 + C^* \rightarrow & C(0) + C(O) \\
C(0) \rightarrow & C^* \\
C^* + NO \rightarrow & CO_x + C(N) \\
C(O) + NO \rightarrow & CO_x + C(N) \\
C(N) + O_2 \rightarrow & CO_x + \frac{1}{2}N_2 \\
C(N) + NO \rightarrow & CO_x + N_2
\end{align}

where \( C^* \) is a vacant carbon active site, and \( C(0) \) and \( C(N) \) are carbon-oxygen and carbon-nitrogen surface complexes, respectively.

De Soete\textsuperscript{27} showed that in some instances the oxygen promotes the NO reduction, but he also found that oxygen can act as an inhibitor for this reaction. In this work it was concluded that the enhancement or inhibition of NO reduction is determined by the CO concentration in the products. The inhibiting effect dominates when CO concentration is low. This was explained by the chemisorption of oxygen on active sites, shielding the carbon sites against NO adsorption.

Generally, the NO/O\textsubscript{2} carbon kinetic experiments are difficult to perform, primarily because the pseudo-steady state assumption is not satisfied (mass loss due to O\textsubscript{2} gasification at high temperatures is significant). Figure 1 shows the kinetics of the NO graphite and NO/O\textsubscript{2} graphite reactions. In this case, the mixture contained 80 to 90 ppm of NO in roughly 2% O\textsubscript{2}, balance helium. Clearly there is a much larger data scatter in the case of the NO/O\textsubscript{2} graphite reaction, which is mostly due to different levels of burn-off of the samples. Different levels of burn-off lead to different surface areas, which is not considered in Figure 1. The reaction rate is enhanced in the presence of oxygen, on average, by a factor of 3. The kinetics of the reaction are very different in the presence of
O₂; there is no clear "break" in the kinetics, which is characteristic of NO carbon reaction. The activation energy of the NO/O₂ graphite reaction (231 kJ/mol) is close to the activation energy of high temperature regime of NO graphite reaction.

From Figure 2, it can be seen that the oxygen enhances the NO-reduction rate also on resin char surface, where the reaction rate is, on average, higher by a factor of 2. Again there is no "break" in the kinetics, at least in the temperature region studied. The activation energy of the NO/O₂ resin char reaction is 53 kJ/mol, which is closer to the activation energy of low temperature regime of NO reduction. It might be surmised that this activation energy corresponds to a process such as generation of active sites, which was earlier hypothesized to control the low-temperature regime of NO reduction.

Figure 3 shows the NO reduction rate as a function of initial O₂ pressure at 500°C, for resin char. Clearly the rate of NO reduction depends on O₂ partial pressure and it appears as though the reactivity goes through a maximum at around 3 kPa. Those results are very similar to those reported by Suzuki et al.²³ and De Soete²⁷; at moderate levels of oxygen (0.5-2%) the concentration dependence is very strong and from there on the effect slows down and even becomes negative. Suzuki et al.²³ reported that this behavior at high oxygen concentrations can be ascribed to the loss of carbon due to oxygen gasification. De Soete²⁷ believes that this is due to the fact that at 2-3% oxygen concentrations the CO₂/CO ratio starts to rise very rapidly and in this suggests screening of the active sites. It seems that both processes could play an important role in the reported behaviour.

During this quarter some reactivity experiments were performed with fly ash samples that contained a considerable amount of carbon. Interest in this field was related to the possible use of fly ash in post-combustion processes, as a reducing agent for NO, but the rates now appear too low at conditions of interest. The Arrhenius plot for the NO fly ash and NO/O₂ fly ash reactions is given in Figure 4, where the reactivities are reported on a mass of carbon basis. Comparison of Figures 1, 2 and 4 shows that the reactivity of fly ash to NO and NO/O₂ is higher than the reactivities of graphite and resin char, at least on a
mass of carbon basis. Surprisingly low activation energy was found for the NO fly ash reaction, only 16.4 kJ/mol, and again the activation energy for the NO/O₂ fly ash reaction was twice as big, 36.2 kJ/mol (ignoring the point at 700°C, which is unusually low due to a loss of carbon). Interestingly, in all three carbonaceous materials studied, the reactivity of NO/O₂ carbon reaction was lower than reactivity of NO carbon reaction at low temperatures. This is not in agreement with Yamashita et al.¹⁹ who found that the reaction rate was considerably increased by an addition of oxygen at 300°C, and even more so when copper catalyst was loaded to the char sample. Additional experiments will be performed in the near future at low temperatures to explore this matter further.

As was mentioned earlier, oxygen gasification is a key step in this reaction system, since it determines the concentration of active sites on the surface. Therefore, the role of O₂ gasification must itself be better understood in these systems, in order to begin to clarify the role of O₂ in NO reduction. To this end, experiments were performed with graphite and resin char, in order to establish their reactivities to O₂ itself. Isothermal reactivity experiments were performed in 2 kPa of O₂. Figure 5 shows that the reactivities of graphite and resin char to O₂ differ by a factor of 20, at least, on a mass of carbon basis. It also seems that there is a oxygen mass transfer limitation at high temperatures. The activation energies of the O₂ resin char and O₂ graphite reactions are 141 kJ/mol and 201 kJ/mol, respectively. The activation energy of the O₂ graphite reaction is similar to that of the activation energy of the NO/O₂ graphite reaction.

It is logical to compare the reactivities on a surface area normalized basis, and this comparison is shown in Figure 6. The results in Figure 6 show that surface area reduces the difference in reactivities of the samples considerably. This suggests that the reaction of resin char and graphite with O₂ occurs over the entire surface area of the carbons at comparable rates (except in the obviously mass transfer limited region).

The mass transfer limitation was verified by the surface area measurements, when surface areas were measured after the gasification in oxygen. At high temperatures (650°C)
the surface area of resin char did not change much from its initial value, whereas at low temperatures (550°C) the surface area increased by a factor of 5 to 9. This clearly supports that the reaction is taking place on the external surface at high temperatures. In the graphite-oxygen reaction, the surface area is not as good of an indicator of mass transfer problem, because the reaction is always taking place on an external surface as the material has little porosity. The surface area depends very strongly on level of burn-off.

During this quarter, the first steps were taken to clarify the mechanistic aspects of NO/O₂ carbon reaction using temperature programmed desorption (TPD) technique. This work is still in progress and those experiments will be continued.

4. Plans for the Upcoming Quarter

Experiments will be continued, using the packed bed reactor and TGA/FTIR system. The NO reduction by CO on quartz surfaces and on carbonaceous materials will be studied further during the next quarter, since these kinetics have not yet been fully explored. The issues with respect to CO₂ have also not yet been fully resolved, and will be the subject of further work. The mechanistic aspects of NO/O₂ carbon reaction will be studied using TGA/FTIR system. Then attention will be turned to the influence of moderate levels of H₂O on NO reduction rate. In addition, the mechanistic implications of the results obtained to date will be examined.

6. References


Figure 1. The effect of O₂ on the kinetics of the NO-graphite reaction.
Figure 2. The effect of O$_2$ on the kinetics of the NO-resin char reaction.
Figure 3. The effect of O$_2$ partial pressure on the NO reduction by resin char. All tests were performed at 500°C in a fixed bed reactor.
Figure 4. The reaction rate constants for NO-fly ash and NO/O2-fly ash reactions, per unit mass of carbon reactant. The fly ash contained about 3.7 weight% of carbon.
Figure 5. O₂-carbon reaction rate, per unit mass of carbon reactant.
Figure 6. O$_2$-carbon reaction rate expressed on surface area basis.