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KINETICS AND MECHANISMS OF NO_x - CHAR REDUCTION

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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 N₂O^{2,6,7}, but that the NO-carbon reactions might also contribute to formation of N₂O^{2,8}. 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.

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 NO_x 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 environments³. The suggestion has been made that the reactions could still be important within the pore structure of the coals, even in a pulverized firing environment¹¹. 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 beds⁸. Of course, it is also the lower temperatures of fluidized bed systems that lead to release of greater amounts of N₂O from these systems, since the N₂O destruction processes have higher activation energies than do formation processes⁷. 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 explored¹². 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}.

2.0 Work During the Present Quarter

An important milestone was achieved during the present quarter, with the submission to the journal *Fuel* of a major review of the kinetics of the NO-carbon system. This invited review incorporated many of the elements presented in previous quarterly reports, together with a significant amount of new information taken from the literature. Since the review is undergoing peer review for publication in *Fuel*, it is not appropriate to present the review in its entirety here. Obviously the review will become available to the public after the review process is complete. Here, only a few key elements of the review will be presented, together with further work on the issue of reaction order with respect to NO.

2.1 Kinetics of the Reaction of Coal Chars with NO

The reaction rate of NO with a wide variety of coal chars is summarized in Figures 1 and 2. The sources of the data are shown in Tables 1 and 2.

A mean value of reactivity was calculated using all of the data in Table 1 (and the high temperature range data of Table 2). This mean reactivity was calculated using the reported kinetic parameters of each study, at the maximum and minimum temperature of each study. Thus each set of results on a different material received equal weight. The result of this averaging process is seen as the regression lines in Figures 1 and 2. The mean activation energy obtained by this method is 133 kJ/mol, for the data set shown in Figure 1. It is seen that this regression procedure produces an activation energy which may be significantly at variance relative to any given data set, but captures the essence of a large amount of data. With only two exceptions, there is at most only about an order of magnitude deviation of actual from mean reactivity on a surface area basis. The actual expression for the rate constant resulting from the averaging procedure may be represented as:

$$k'' [\text{g}_{\text{NO}}/\text{m}^2 \cdot \text{hr} \cdot \text{atm NO}] = 5.5 \cdot 10^6 \exp (-15939/T) \quad (1)$$

There is no consistent variation of coal reactivity with rank in Figure 1. This is perhaps not surprising, since there are many factors not explicitly represented in that figure that would tend to influence the reactivity. These factors include the severity of heat treatment and the impurity content. With respect to the former, it has been earlier reported that there is a complicated dependence of reactivity on heat treatment temperature^{21,22}.

Figure 2 provides data on several more coal chars, not included in Figure 1. The reason that these results are presented separately is that they all exhibit the two-regime behavior discussed previously for other types of carbons. The regression line from Figure 1 is also shown in Figure 2, and indicates that these samples have reactivities that cluster about the regression line, though a few

highly heat treated samples (1273 K for 2 hours) from this laboratory show significantly lower reactivity. Thus there is nothing in the measured levels of reactivity that can be used to explain why some samples exhibit the broken Arrhenius plot and others do not. Nor is the broken Arrhenius behavior attributable to the presence or absence of significant amounts of catalyst, since it is observed for both highly impure coal chars as well as for relatively pure graphites. A mean reactivity was given above for all coal samples, for the high temperature regime. Using only the low temperature regime results of Figure 2, a similar correlation may be determined for this regime:

$$k'' [\text{g}_{\text{NO}}/\text{m}^2 \cdot \text{hr} \cdot \text{atm NO}] = 0.191 \cdot \exp (-3464/T) \quad (2)$$

Also notable from Fig. 2 is a disagreement in results obtained in this laboratory on identical Wyodak coal char samples, using two different measurement techniques (a third Wyodak sample, prepared and studied earlier by Teng et al.²³, cannot be directly compared because it was neither identically prepared nor measured). The reactivities in the low temperature regime are again quite comparable, using both the TGA and fixed bed techniques. As in the case of the comparison of resin char results presented earlier, here the reactivities derived from fixed bed results in the high temperature regime are also consistently higher than those derived using the TGA technique. Again, these results indicate a potential difficulty in interpreting the results of fixed bed reactor studies, in which *product* gases of NO reduction have a good opportunity to contact NO in the presence of the char bed. Evidence will be presented below to support a role of char-catalyzed NO reduction by CO in such systems. We believe that such reactions might play a significant role in many fixed bed studies, particularly with highly reactive materials, such as coal chars. To the extent that contact between product gases and char bed varies from study-to-study, this can also contribute to apparent data scatter. This issue has been further explored experimentally.

2.2 Experimental

A quartz packed bed reactor tube of 4 mm internal diameter and 500 mm overall length was used. 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. The reactor was heated by a McDanel electrical tube furnace and a chromel-alumel thermocouple was placed outside the reactor tube for temperature measurements. Special care was taken about to verify that temperature measurements made outside the bed corresponded to those made inside of the reactor .

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 1173K for 1-2 hours in He) to remove surface oxides. In the study of pyrolysis conditions the surface cleaning step was omitted. Nitric oxide/helium mixtures of the desired concentration levels were prepared using a KIN-TEK precision calibration system. The helium (99.9% from the cylinder) was purified to a higher degree by the use of an additional cryogenic trap, maintained at 77K and packed with Porapak Q. The desired NO/He mixtures (10-300 ppm of NO in He) were obtained by controlling the flow rate of helium, and both the absolute temperature of the permeation membrane and the NO partial pressure in KIN-TEK calibration system.

During the reactivity measurements, the product gases were continuously analyzed for NO and NO₂ using a chemiluminescence analyzer. The other product gases as CO₂, CO can be analyzed by gas chromatography, but this was not done here.

Specific surface areas of char samples were determined by the N₂ BET method at 77 K. 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 573 K for 3 hours.

Results for resin char experiments, using this device, were reported in the 5th quarterly. The graphite for the present packed bed measurements was prepared from graphite rods from Great Lakes Carbon, and had an ash content of 0.06%. The particles were ground and sieved to 180-290 μ m size.

2.3 Results of Experiments Establishing the Order of Reaction with Respect to NO, in the Presence of CO

In a packed bed reactor, if the reaction is first order with respect to NO, the reaction rate constants can be calculated using the design equation for a packed bed reactor

$$k = -\frac{1}{\tau} \ln[1 - X] \quad [\text{hr}^{-1}] \quad (3)$$

where τ is the residence time, in hours, and X is the extent of NO conversion. This expression shows that for a truly first order reaction, conversion is independent of the absolute NO concentration.

Figure 3 shows the fractional conversion of NO as a function of initial NO concentration, for two different cases. In one case, the feed contains no CO, and in the other case, the feed contains approximately 275 ppm of CO. Clearly fractional conversion is a strong function of initial NO concentration at only in the presence of CO. This means, further that the rate is fractional with respect to NO. In the absence of CO, there is one point at very low NO concentration that disagrees with first order kinetics, but otherwise first order behavior is strongly supported. It is possible that when NO pressure gets very low, that a different rate limiting step becomes important, but it is at present unclear how much significance can be attached to that one departure from first order behavior.

Thus, as reported in the fifth quarterly, we again see strong support for the position that reports of fractional order kinetics with respect to NO partial pressure may be artifacts of performing the reaction in CO-containing atmospheres. The CO itself may be generated as a product of the reaction of NO with carbon:

This reaction may be followed in a packed bed (in which products contact the reactive medium further) by:

The reaction rate expression should in this case contain two terms

$$r = k_1 \cdot P_{\text{NO}}^n + k_2 \cdot P_{\text{NO}}^m \cdot P_{\text{CO}}^l \quad (4)$$

where k_1 and k_2 are reaction rate constants for reactions (R1) and (R2), respectively, and n , m and l are reaction orders with respect NO, NO and CO partial pressures, respectively. The apparent order with respect to NO may easily be fractional, in such a case. The reason that the effect of product CO is not seen in the experiments with graphite might be that the graphite is very unreactive, and the partial pressure of the CO product would be quite low throughout the packed bed.

Thus any reports of fractional order with respect to NO must be viewed with caution, particularly if obtained in a packed bed type of reactor. It appears that the weight of evidence favors a first order primary attack of NO on carbon, followed by a further carbon surface-catalyzed reduction of NO by CO. The kinetics of this latter step have not yet been firmly established.

3.0 Plans for the Next Quarter

The intention is to examine the effect of other added gases on the kinetics of NO-carbon

reactions. The gases to be explored include, in addition to CO, other typical components of flue gas, i.e., oxygen, CO₂ and H₂O. There is still much uncertainty in the literature about the effects of these added gases, though generally O, like CO, appears to enhance the rate of reduction of NO.

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Table 1. Key for Figure 1.

Symbol	Carbon type	Reactor	Temperature Range [K]	NO pressure [kPa]	Activation en. kJ/mol	Reaction order	Surface Area [m ² /g]	Reference
	Montana Lignite Coal Char	Flow Reactor	1250-1750	0.05-0.65	137	1	126-234	26
	Bituminous Coal Char	Fixed Bed	1073-1173	0.03-0.1	184.6	0.58	32.6	37
	Brown Coal Char	Fixed Bed	1073-1173	0.03-0.1	184.6	0.52	194.5	37
	Petroleum Coke	Fixed Bed	1073-1173	0.03-0.1	196.2	0.49	5.1	37
	Lignite Coal Char	Fixed Bed	673-1223	0.06-0.32	116	0.23	300	38
	Gardanne Subbituminous Coal Char	Fixed Bed	673-1223	0.06-0.32	111	0.22	334	38
	High-Volatile Bituminous Coal Char	Fixed Bed	673-1223	0.06-0.32	167	0.43	263	38
	Blanz Anthracite Char	Fixed Bed	673-1223	0.06-0.32	181	0.36	294	38
	High-Volatile Bituminous Coal Char	Fixed Bed	673-1023	0.002-0.04	120	0.6	-	28
	Coke deposited over CaO	Fixed Bed	673-972	0.179	105	-	-	24
	Coal Char + KOH	Fixed Bed	873	0.4	195	-	1790	25
	Montana Lignite Coal Char	Fixed Bed	700-1180	0.4	124	-	54.7	36
	Montana Lignite Coal Char	Fixed Bed	1250-1750	0.95	147	-	175	27
	High-Volatile Bituminous Coal Char	Fixed Bed	973-1223	0.05-0.15	167.7	1	1.7	35
	Demineralized High-Volat. Bit. Coal Char	Fixed Bed	973-1223	0.05-0.15	151.8	1	1.7	35
	Low-Volatile Bituminous Coal Char	Fixed Bed	973-1223	0.05-0.15	154	1	2.85	35
	Demineralized Low-Volat. Bit. Coal Char	Fixed Bed	973-1223	0.05-0.15	138.1	1	3.47	35
	Pennsylvania Anthracite Char	Fixed Bed	800-1250	0.1-0.15	101	-	80	33,34
	Ruhr Low-Volatile Bituminous Coal Char	Fixed Bed	800-1250	0.1-0.15	81	-	80-88	33,34
	North Dakota Lignite Coal Char	Fixed Bed	800-1250	0.1-0.15	43	-	200	33,34
	Utah Bituminous Coal Char	Fixed Bed	800-1250	0.1-0.15	101	-	145	33,34
	South African Coal Char	Fixed Bed	800-1250	0.1-0.15	74	-	0.85	33,34
	W. Virginia 'Pocahontas' Coal Char	Fixed Bed	800-1250	0.1-0.15	170	-	1.3	33,34
	W. Virginia 'Cedar Grove' Coal Char	Fixed Bed	800-1250	0.1-0.15	165	-	0.55	33,34
	Least Squares Regression Line	-	773-2000	-	99	-	-	-

Table 2. Key for Figure 2.

Symbol	Carbon type	Reactor	Temperature	NO pressure	Activation energy, kJ/mol		Reaction	Surface Area	Reference
					Low temp.	High temp.			
—△—	Wyodak Coal Char	TGA	773-1073	1.0-10.1	70	127	-	213-333	23,32
—■—	Montana Lignite Coal Char	Fixed Bed	723-1173	0.05-1.0	62	168	1	402	30
—▣—	Coal Char + KOH	Fixed Bed	673-1023	0.4	48	127	-	1790	25
—●—	Taiheiyo Coal Char	Fixed Bed	773-1118	0.03-0.20	68.1	245	1	800-1200	31
—□—	Anthracite Char	CSTR/PFR	848-1223	0.51	46.8	193.5	-	-	29
—◆—	Wyodak Coal Char	TGA	773-1173	1.0-8.1	43	109	-	681-1286	this study
—◇—	Wyodak Coal Char	Fixed Bed	723-1023	0.001-0.03	38	198	0.36	378-1000	this study
—○—	Lignite Char	Fixed Bed	723-1073	0.3	87	180	-	190	39
—	Least Squares Regression Line	-	773-1500	-	-	99	-	-	-

Figure 1. A summary of first order rate constants for the reaction of pure NO with coal chars. The rate constant k'' is shown on a surface area basis. The key to the symbols is shown in Table 1. The thin line without data points shows the mean of the data for coal chars in the high temperature regime (see text).

Figure 2. A summary of first order rate constants for the reaction of pure NO with coal chars. The rate constant k'' is shown on a surface area basis. These data were selected to show the two-regime behavior of the rate constants. The key to the symbols is shown in Table 2. The thin line without data points shows the mean of the data for coal chars in the high temperature regime (see text).

Figure 3. The effect of CO on the apparent order of the NO-graphite reaction. All tests were performed at 1073 K in a fixed bed reactor. Open diamonds- results in the absence of added CO; closed squares- results in the presence of 275 ppm of CO.