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KINETICS AND MECHANISMS OF NO_x - CHAR REDUCTION

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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_2O 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_2O problem. This is in part because earlier estimates of the importance of N_2O 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_2O 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_2O[2,6,7], but that the NO-carbon reactions might also contribute to formation of N_2O[2,8]. The precise role of carbon in N_2O 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_2O 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_2O-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_2O 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_2O from these systems, since the N_2O 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. Experimental

A DuPont thermogravimetric analyzer (TGA) is used for the char reactivity studies. A schematic of the apparatus is shown in Fig. 1. The temperature and mass are recorded as function of time, using a Macintosh computer and software for simultaneous apparatus control and data acquisition. Samples of 5-35 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 3 mm from the sample.

The volume of the DuPont TGA is very small and gas consumption during experiments can be significant, therefore we are performing reactivity measurements with continuous flow of gases through the TGA. As nitric oxide is known to be a strong oxidizer, to avoid any contact of NO with the balance mechanism the part of balance case that houses it is purged with a pure helium stream. This is schematically indicated in Figure 1. The reactive nitric oxide/helium mixture is introduced near the sample itself. The TGA system was designed to be gas-tight to avoid possible air leaks into the system, and it can be quickly evacuated and filled with gases through a manifold.

All samples were outgassed prior to each run by a one hour vacuum pumping on the TGA at room temperature. This was followed by thermal surface cleaning (at 1273K for 1-2 hours in He) to remove surface oxides. The mixture of nitric oxide in helium (9.37 vol%) was obtained from a commercial source (Matheson Gas Products, Inc.). High purity helium is used to dilute the nitric oxide helium mixture. An additional cryogenic trap, maintained at 77K and packed with Porapak Q, is provided between the helium supply and the helium flow controller to eliminate traces of impurities in the helium. The desired NO/He mixtures (1-8 vol% of NO in He) were obtained by controlling the relative flow rates of the cylinder NO-helium mixture and the pure helium.

Products formed during the gasification experiments can be analyzed by gas chromatography or FTIR spectrometry. Since such experiments have not been performed yet during this quarter, these procedures will not be discussed here.

Specific surface areas of char samples were determined by the N_2 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.

The carbonaceous solids used were resin char, graphite, coconut char and a Wyodak coal char. The resin char samples were derived from phenol-formaldehyde resins made in-house. The coal char was also prepared in-house from the Wyodak sample from the Argonne Premium Coal Sample Program. The chars were prepared by a two hour pyrolysis, in inert gas, at a temperature of approximately 1223 K. The graphite was purchased from the AESAR/ Johnson Matthey Company, and the coconut char was purchased from Fisher Scientific Corporation. Neither of these latter two samples was treated any further, except for surface cleaning.

3. Results and discussion

As was noted in the last report, carbons derived from different original materials show quite similar behaviors, in terms of the trends, but there are significant differences in actual reaction rates, see Figure 2. It was shown that the spread of the reaction rate data from different studies, when expressed on a mass of carbon reactant- or surface area-basis, was almost the same. Since comparing results from different studies often meant comparing results obtained at quite different NO pressures, it was necessary to compare true rate constants, rather than rates. This generally meant dividing the rates by the partial pressure of NO. This assumed a first order NO dependence, as had been reported earlier. The global order of reaction with respect to NO was, again, here verified to be unity, in experiments in which the NO partial pressure was varied between 1.0 and 6.1 kPa, see Figure 3.

The suggestion was made in the last quarterly report that the gasification reaction might occur primarily outside of the microporous network, on the surfaces of large pores and on the external surface of the char. Experiments were performed this quarter to further test this hypothesis.

The different carbons described above were used for comparative reactivity measurements. Reactivity profiles for all the carbons studied, expressed on mass of carbon reactant basis are presented in Figure 4 and the same results on a surface area basis are shown in Figure 5. These experiments were all carried out under the same experimental conditions (NO partial pressure 2 kPa). It should be noted that all of them exhibit quite similar qualitative behavior (with the exception of graphite, which is discussed subsequently). That is, the curves all show a "break" at around 900 K, where a significant change in the mechanism of the NO- carbon gasification reaction has been earlier found to occur. This break point temperature is similar to others reported in literature.[23-25]

In the previous study of the mechanism and the kinetics of NO- carbon reaction in this laboratory, it was concluded that the kinetics of this reaction system can be divided into two temperature regimes, one above and the other below the break point. In the lower temperature regime, the process is governed by a distribution of activation energies, and in the higher temperature regime, the apparent activation energy exhibits a relatively constant value. The activation energies for different carbons found in this study (see Table 1) are much lower and reactivities (Figures 4 and 5) are much higher, than those found earlier in this laboratory. The activation energy had earlier been reported to be 60-80 kJ/mol in the low temperature regime and 180 kJ/mol in the high temperature regime, for the same resin char as used here.

The difference in activation energies and reactivities appears to arise in large part from the different methods now being used to conduct the reactivity studies. The difference is that we are now cleaning the carbon surface (one hour in He at 1273 K) after every isothermal reactivity run. Earlier, the temperature had been merely changed from one value to another, without any surface cleaning. The reason for the effect of the procedure on results is still unclear. It is undoubtedly related to the transient behavior of the oxides on the surface. This is especially strongly suggested by the major difference in rates between our earlier results (Teng et al., in Figure 5) and our present results on resin char in the low-temperature, desorption rate-controlled regime. There must be a significant difference in the oxide populations on the surface during the two different types of tests. This will be discussed further in a later report. For the remainder of the report, the difference between the old and new resin char results will be disregarded, and attention turned to the question of comparability of different chars, and the role of surface area in reaction.

Figure 4 shows that there exist large differences in reactivity of different carbons, when expressed on a mass of carbon reactant basis. The results in Figure 5 shows that surface area accounts for the differences in reactivity rather well. This indicates that the reaction of carbons with NO, under the experimental conditions of present study, seems to occur over the entire surface area of the carbon. This appears to be true of an enormous variety of materials, ranging from those with low catalytic impurity levels (resin char) to those with significant mineral content (Wyodak). Thus the earlier observed wide variability in surface area-corrected rate constants, for chars derived from different materials, must have its origin in how the materials were prepared or how the experiments were performed.

Graphite is seen to exhibit somewhat unique behavior in Figure 5. Graphite gasification with NO has also been studied by Chan et al.[23] and Chu & Schmidt[26]. Chu and Schmidt used scanning tunneling microscopy to study carbon/NO reaction kinetics. The basic idea was 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 suggested that the reaction initiates on point defects. The growth rates gave the gasification rates, and these were studied at temperatures between 800 to 950 K. Their activation energy 72-78 kJ/mol is similar to our low temperature regime activation energy for graphite. They did not find any break in kinetics under their experimental conditions. Our results strongly suggest that they might not have found any because the break point in kinetics is higher for graphite than for the other carbons.

Chan et al.[23] studied the NO- graphite reaction in a fixed bed reactor at temperatures between 950 to 1200 K. They reported an activation energy 238 kJ/mol, which is in good agreement with our high-temperature region activation energy value. They did not report a break point in the reaction kinetics for the NO- graphite reaction, although they saw an obvious break in NO- coal char reaction kinetics at around 900 K. In this case, the lowest temperature that they examined might have been quite close to the break point, and they might have missed it for that reason.

From our study of NO- graphite kinetics we found that the break in kinetics occurs at somewhat higher temperatures (around 1050 K) for the graphite than for the other chars. Moreover, the activation energies in both temperature regimes are greater than the corresponding values for other chars, see Figure 5 and Table 1. The NO- graphite reaction will receive more attention in future work, but at the moment we believe that the movement of the break point toward higher temperatures is due to the lower concentration of active sites in graphite than in other chars. The reasons for this are, again, not fully understood. It might be surmised from the results that have been obtained that the dissociative chemisorption sites available in graphite are fewer in number and different in nature than the same types of sites in more disordered chars. Therefore their influence in graphite gasification is felt only at somewhat higher temperatures than it is in more disordered chars.

4. Plans for the Upcoming Quarter

The TGA apparatus will be fully rebuilt to accommodate the FTIR analysis of the product gases. During the time that this apparatus is not available, some tests will be performed using the packed bed apparatus. This device needs to be made fully operational. In addition, the mechanistic implications of the results obtained to date will be examined.

5.0 References

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Table 1. Specific surface areas and activation energies of carbons studied.

Material	Specific Surface Area [m^2/g]		Activation Energy [kJ/mol]	
	Unreacted	Reacted	Low Temp.	High Temp.
Resin Char	525	878	30-40	140
Graphite	17	49-326	53-79	185-221
Coconut Char	3291	2682	42	120
Wyodak Coal Char	681	1286	43	109

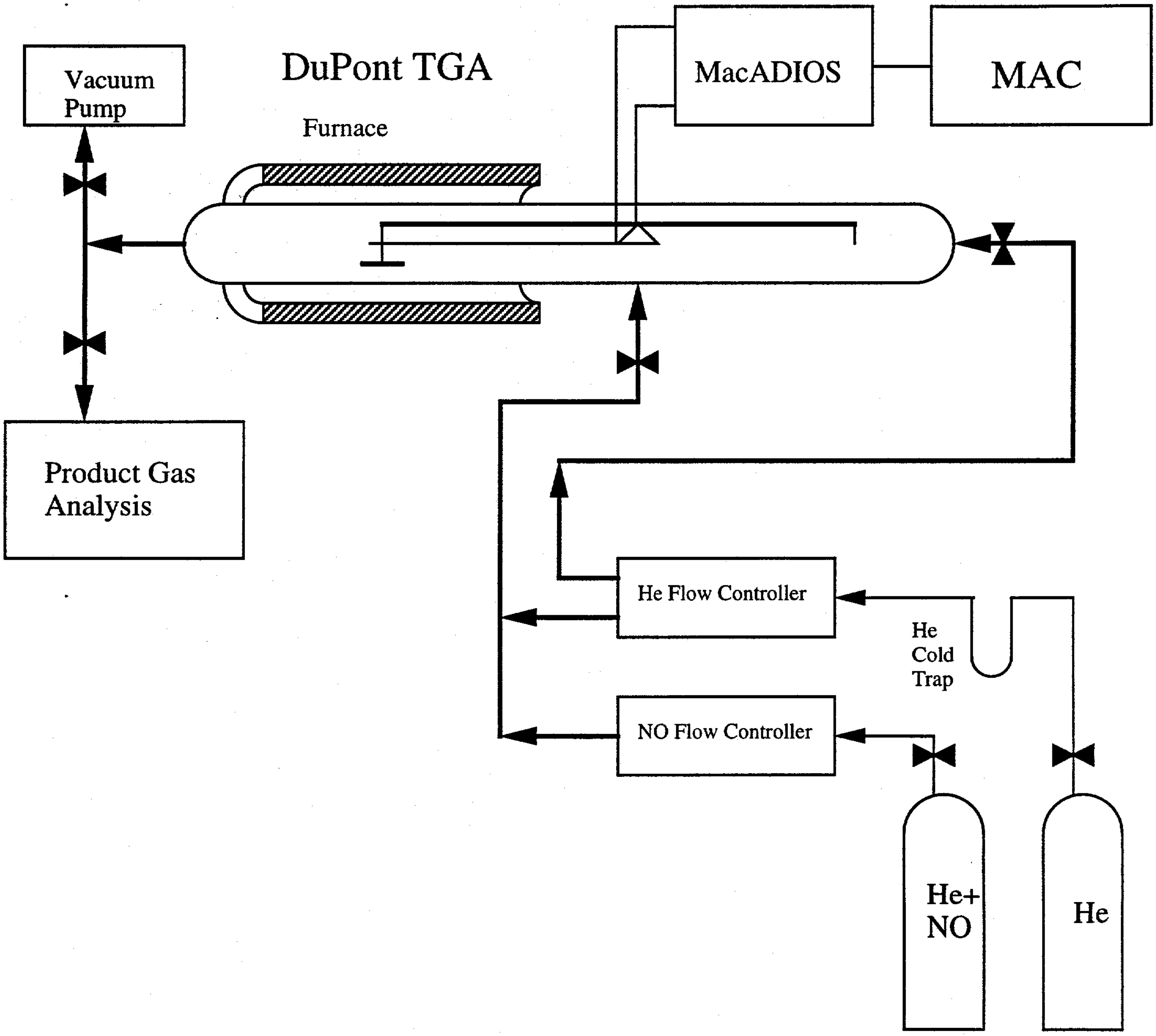

Figure 1. Schematic of TGA apparatus.

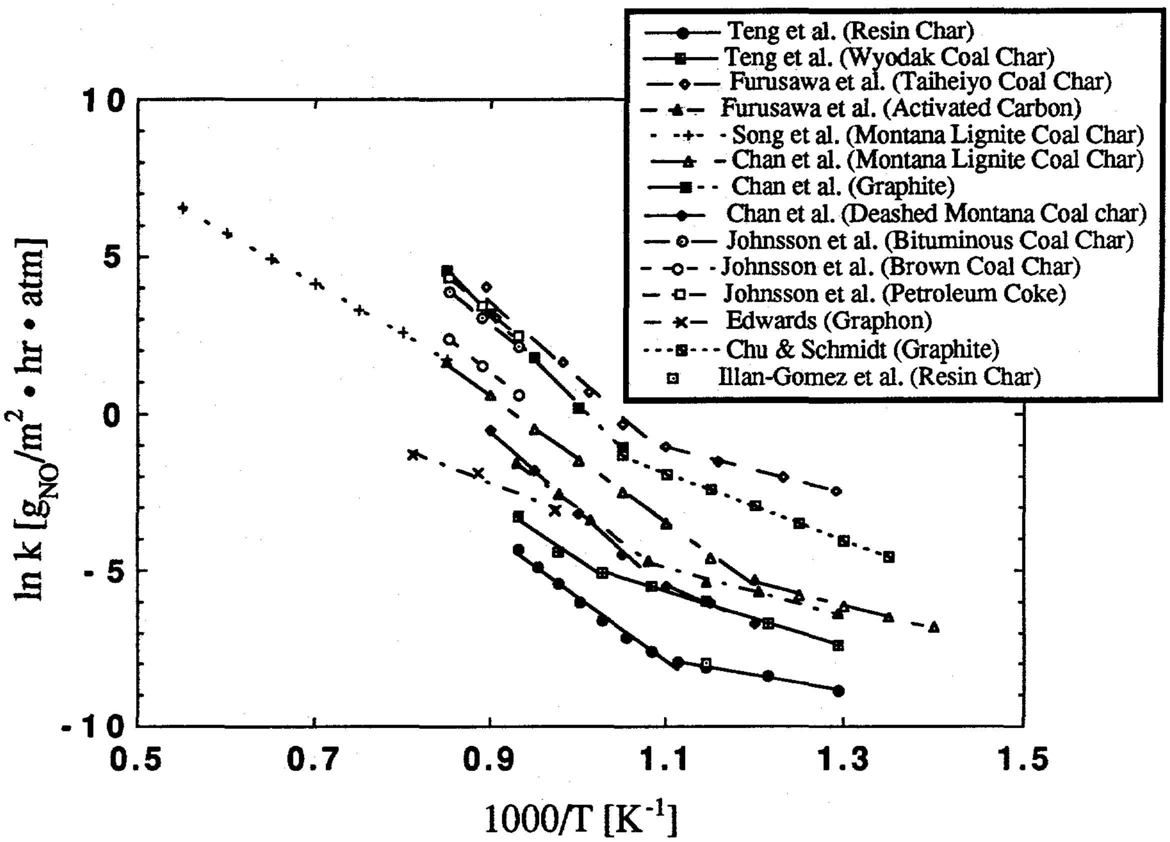

Figure 2. NO-carbon reaction rate constant expressed on a surface area basis.

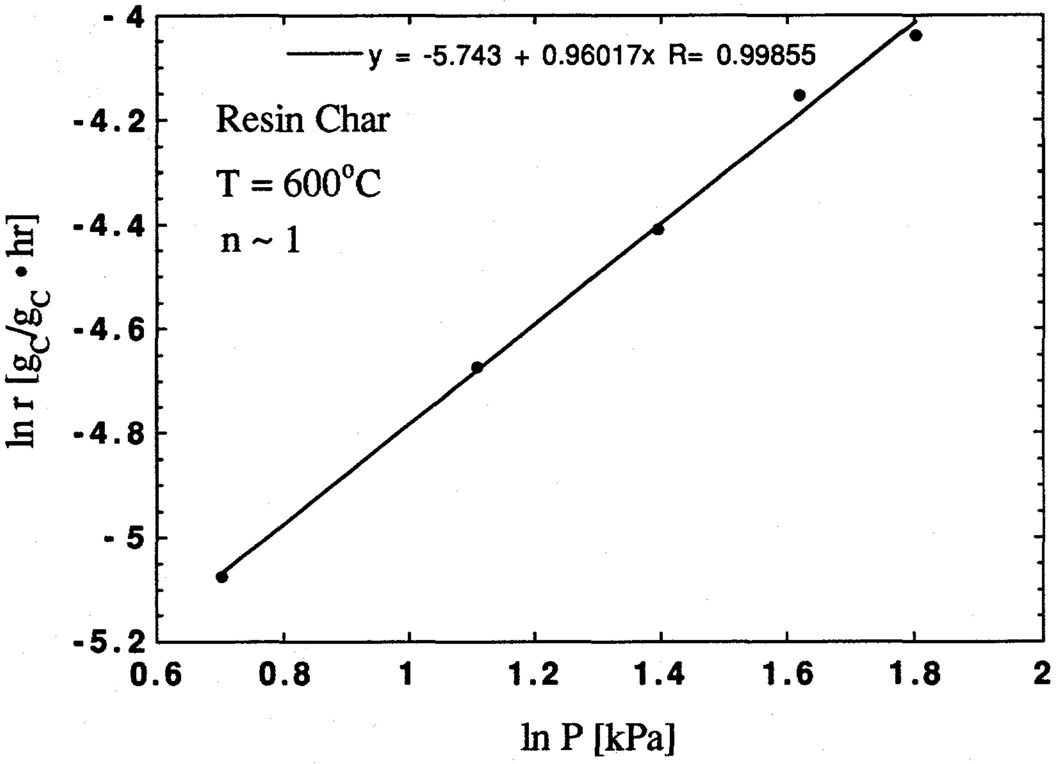

Figure 3. Reaction rate vs. NO partial pressure, showing overall first order behavior.

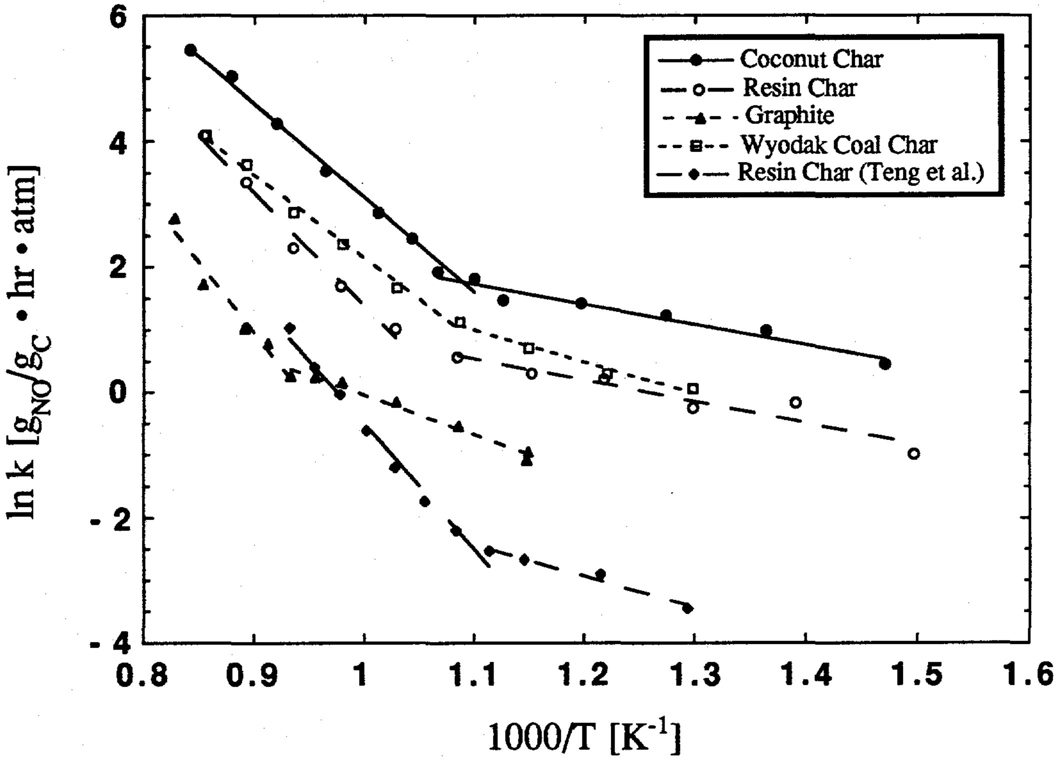

Figure 4. NO-carbon reaction rate constant, per unit mass of carbon reactant.

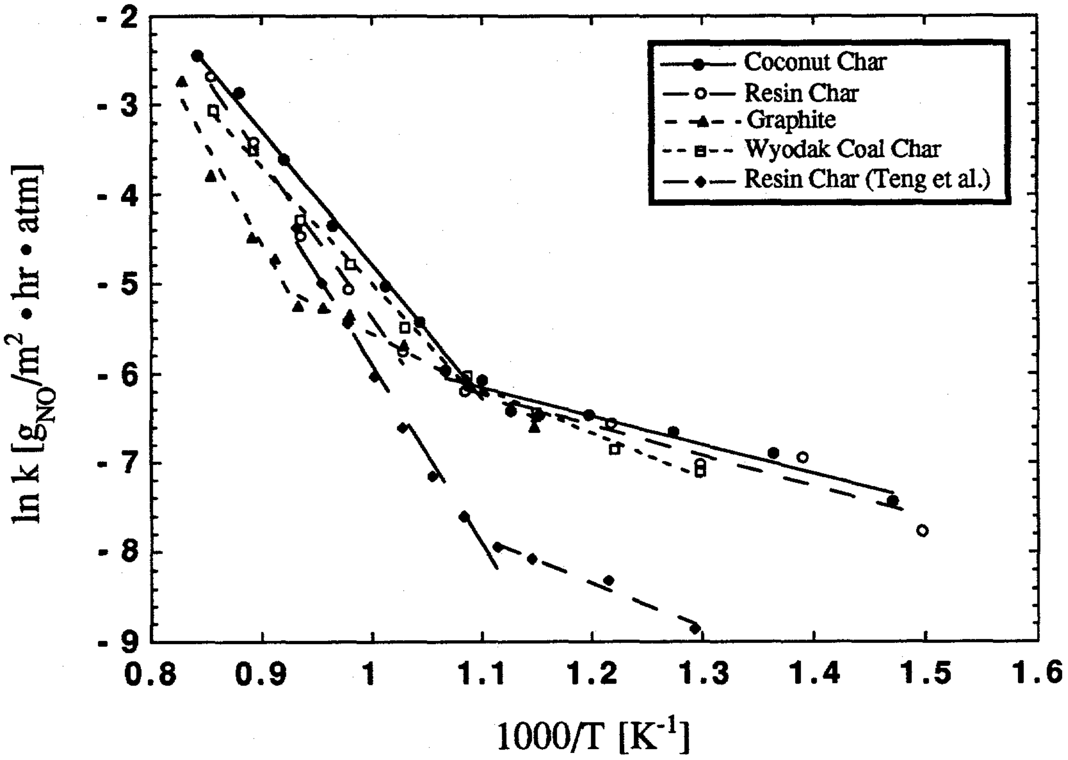

Figure 5. NO-carbon reaction rate constant expressed on a surface area basis.