DOE / PC94218-4

KINETICS AND MECHANISMS OF NOx - CHAR REDUCTION

E. M. SUUBERG (PRINCIPAL INVESTIGATOR)
W.D. LILLY (STAFF)
I. AARNA (Ph.D. STUDENT)

DIVISION OF ENGINEERING
BROWN UNIVERSITY
PROVIDENCE, RI 02912
TEL. (401) 863-1420

RECEIVED
USDOE/PETC
95 AUG 23 AM 10: 38
ACQUISITION & ASSISTANCE DIV.

QUARTERLY TECHNICAL PROGRESS REPORT
1 MAY, 1995 - 31 JULY, 1995

PREPARED FOR:
U. S. DEPT. OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 10940
PITTSBURGH, PA 15236

DR. ROBERT GROSS
TECHNICAL PROJECT OFFICER

"US/DOE Patent Clearance is not required prior to the publication of this document"

DLC

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 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 significant amount of time has been devoted during this quarter to preparing the packed bed apparatus, which will be described below.

A schematic of the apparatus is shown in Fig. 1. A quartz packed bed reactor tube of 4 mm internal diameter and 500 mm overall length was used. A bed of 100-200 mg (in a predetermined length of 10-30 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 experimental conditions studied are given in Table 1. 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. 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 (200-300 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 NO_2 using a chemiluminescence analyzer. The other product gases as CO_2, CO can be analyzed by gas chromatography, but this was not done 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. Specific surface areas of different carbons are given in Table 2. It should be noted that the materials are highly microporous. The activated charcoal in particular gives surface areas that approach the theoretical maximum of every carbon atom exposed to the surface. This, of course, is not the case, but is rather an artifact of the pore filling. This has significance in the interpretation of results shown below.

The carbonaceous solids studied to date were resin char, graphite, coconut char and a Wyodak coal char. The resin char (180-290μm) samples were derived from phenol-formaldehyde resins made in-house. The coal char (150-212μm) 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 (110 μm mean particle size) was purchased from the AESAR/ Johnson Matthey Company, and the coconut char (180-231μm) 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, there exist large differences in reactivity of different carbons, when expressed on a mass of carbon reactant basis, see Figure 2. Some reactivity measurements were performed during this quarter using the packed bed reactor. The reaction rate constants were calculated, by assuming a first-order kinetics (it was verified to be unity in the last report), using a design equation for packed bed reactor

$$k = -\,1/\tau \bullet \ln(1-X) \qquad [\mathrm{hr}^{-1}] \qquad (1)$$

where τ is the residence time, hr, and X is the extent of reaction. The conversion of this rate constant to our bases can be accomplished by

$$k' = k\, M_{NO}/(\rho_c RT) \qquad [g_{NO}/g_c\text{-hr-atm}] \qquad (2)$$

where M_{NO} is the molecular weight of NO (30 g/mol), ρ_c is the bed density of the char (approximately 0.7 g/cm^3), R is the gas constant (82.06 cm^3-atm/mol-K), and T is the temperature.

Reactivity profiles for all the carbons studied from the TGA and packed bed experiments, expressed on mass of carbon reactant basis are presented in Figure 2. The activation energies for different carbons from different experiments found in this study are given in Table 2. It should be noted that all carbons exhibit quite similar qualitative behavior (with the exception of graphite). 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].

A good agreement between our TGA and packed bed reactor results is seen in Figure 2. these results clearly support our earlier findings that significant differences in actual reaction rates reported in the literature are not attributable use of different systems, but probably arise from the unrecognized differences in procedures used to conduct the reactivity studies.

Our packed bed reactor results also erase all doubts about reaction order. Although reaction orders between 0.42 and 0.73 have been reported[26,27], here there is no doubt as to order being unity, because the NO concentrations used in the packed bed experiments were 100 times smaller (200-300 ppm) than in TGA experiments (2%). In spite of this wide variation in concentration, the results from both systems are seen to be very close in Figure 2.

A higher activation energy was found in the high temperature region for resin char 2 studied by the packed bed technique, as opposed to the TGA technique (see Table 2). This higher activation energy is, in fact, similar to activation energies found from other packed bed reactor studies by other workers[23,24]. The reasons for the slight difference between the two techniques is not yet clear. In the high temperature regime CO becomes a more important product, and it is well known that heterogeneous NO reduction at the char surface is enhanced in the presence of CO[23,26]. It might be that the CO-enhanced reactions have an influence on our results in the high temperature regime, though it is unclear why there is no evidence of this with all materials. This issue will be studied further during the next quarter.

It is logical to also compare the reactivities on a surface area normalized basis, and this comparison is shown in Figure 3. The results in Figure 3 shows that surface area reduces the observed spread in reactivities somewhat. This suggests 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. There is a relatively narrow range of reactivities for an enormous variety of materials, ranging from those with low catalytic impurity levels (resin char) to those with significant mineral content (Wyodak). This is somewhat surprising. The earlier reported (2nd quarterly report) 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 in some as-yet unclear aspect of how the experiments were performed. We suspect that sample preparation might be a key, in that all materials studied here have had fairly extensive heat treatment, or are inherently fairly highly ordered.

Interestingly, the comparison of our results from the TGA and packed bed reactors is seemingly made a bit worse on a surface area basis. The reasons for this are unclear. In the case of the coconut char, which has very high nominal surface areas, the problem may have to do with the interpretation of the N_2 sorption results in terms of surface, as opposed to micropore filling. The true reactive surface areas might be closer than the measured "surface areas" would imply.

Using the results from Figure 3, the reaction rate constant for NO reduction on a surface area basis can be described by two Arrhenius equations

$$k_1 = (8.863 \pm 0.460) \cdot 10^{-2} \cdot \exp[-(3440 \pm 180)/T] \quad [g_{NO}/m^2\text{-hr-atm}] \quad (3)$$

$$k_2 = (1.226 \pm 0.026) \cdot 10^{4} \cdot \exp[-(14390 \pm 300)/T] \quad [g_{NO}/m^2\text{-hr-atm}] \quad (4)$$

in the low (400-650°C) and high (650-950°C) temperature regions, respectively. Due to the different behavior of graphite and resin char 2, these results were excluded from the fitting procedure.

The different behaviors of resin char 1 and 2 is of unclear origin. Resin char 2 shows a much higher reactivity on mass of carbon basis, and the break point between low and high temperature regimes occurs at higher temperature (700°C). It might be explained by pore structure differences. Resin char 1 came from the same starting resin as did resin char 2. Resin char 1 is a char used by Teng et al.[25] in their study five years ago and increased in surface area from 220 to 520 m^2/g during experiments at that time. Resin char 2 had not been used before and it had almost no surface area before these experiments. This means that the difference between these materials comes about as a consequence of surface area development during use. Thus far, no explanation has been uncovered as to the origin of the different extents of "activation". This is clearly a significant issue to be explored further.

4. Plans for the Upcoming Quarter

Experiments will be continued, using the packed bed reactor. Specifically, packed bed experiments of the kind performed here will be performed on graphite and on Wyodak coal char, to establish the generality of the trends uncovered thus far. Then attention will be turned to the influence of added gas components on NO reduction rate. These added components will include those normally expected to be present in combustion products, including low levels of O_2 and CO, and moderate levels of H_2O. In addition, the mechanistic implications of the results obtained to date will be examined.

Hopefully, the TGA/FTIR system will be ready and some preliminary experiments will be performed.

5. References

1. Johnson, G.M., Smith, M.Y., Mulcahy, M.., 17th Symp. (Int.) on Comb., Combustion Institute, 647 (1979).
2. deSoete, G.G. 23rd Symp. (Int.) on Combustion, The Combustion Institute, 1257 (1990).
3. Aho, M., Rantanen, J., and Linna, V., Fuel, 69, 957 (1990).
4. Aho, M. and Rantanen, J., Fuel, 68, 586 (1989).
5. Houser, T., McCarville, M., and Zhuo-Ying, G., Fuel, 67, 642 (1988).
6. Wojtowicz, M., Pels, J., Moulijn, J., Proc. 1991 Int. Conf. Coal Sci., p 452, Butterworth, Oxford, 1991.
7. Wojtowicz, M., Oude Lohuis, J., Tromp, P., Moulijn, J., Int. Conf. Fluid. Bed Comb., 1013, 1991.
8. Åmand, L., Leckner, B., and Andersson, S., Energy and Fuels, 5, 815 (1991).
9. Muzio, L. and Kramlich, J., Geophys. Res. Lett., 15, 1369 (1988).
10. Pereira, F., Beer, J., Gibbs, B. Hedley, A., 15th Symp. (Int.) on Comb., Combustion Institute, 1149 (1975).
11. Hahn, W. and Shadman, F., Comb. Sci. and Tech., 30, 89 (1983).
12. Hjalmarsson, A.M., NOx Control Technologies for Coal Combustion, IEA Coal Res. Rept. IEACR/24, 1990.
13. Inui, T., Otowa, T., and Takegami, Y., I &EC Prod. Res. Dev., 21, 56 (1982).
14. Stegenga, S., Mierop, A., deVries, C., Kapteijn, F., and Moulijn, J., Proc. 19th Biennial Conf. on Carbon, p. 74, The American Carbon Society, 1989.

15. Mochida, I., Ogaki, M., Fujitsu, H., Komatsubara, Y., and Ida, S., Fuel, 64, 1054 (1985).
16. Richter, E., Kleinschmidt, R., Pilarczyk, E., Knoblauch, K., and Juntgen, H., Thermoch. Acta, 85, 311 (1985).
17. Lai, C.-K. S., Peters, W. A. and Longwell, J. P., Energy & Fuels, 2, 586(1988).
18. Illán-Gómez, M., Linares-Solano, A., Salinas-Martinez , C., Calo, J.M., Energy and Fuels, 7, 146 (1993).
19. Yamashita, H., Tomita, A.,Yamada, H., Kyotani, T., and Radovic, L, Energy and Fuels, 7, 85 (1993).
20. Okuhara, T. and Tanaka, K., J. Chem. Soc., Faraday Trans.-1, 82, 3657 (1986).
21. Taylor, R.W. and Morris, C.J., ACS Div. Fuel Chem. Prepr., 29(3), 277 (1984).
22. Personal Communication, Prof. I. Opik, May, 1992.
23. Chan, L. K., Sarofim, A. F. and Beer, J. M., Combustion and Flame, 52, 37/45 (1983).
24. Furusawa, T., Kunii, D., Osuma, A. and Yamada, N., International Chemical Engineering, 20, 239(1980).
25. Suuberg, E. M., Teng H. and Calo, J. M., Energy and Fuels, 6, 398 (1992).
26. Johnsson, J.E., and Dam-Johansen, K. 11th International Conference on Fluidized Bed Combustion, p. 1389, New York, (1991).
27. Schuler, J., Baumann, H., and Klein, J. 1987 Int. Conf. Coal. Sci., p. 857, Elsvier, (1987).
28. Berger, A., and Rotzoll, G., Fuel, 74, 452 (1995).

Table 1. Experimental parameters.

Material	Amount (mg)	Particle size (μm)	Flowrate (cc/min)	Inlet NO conc.(ppm)	Char Bed Length (cm)
Coconut Char	84	180-231	120-125	200-300	1.1
Resin Char	224	231-290	90-100	200-300	2.1

Table 2. 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 1 (TGA)	525	878	30-40	140
Resin Char 2 (TGA)	-	211	40	135
Resin Char (Packed Bed)	-	267	27	168
Graphite (TGA)	17	49-326	53-79	185-221
Coconut Char (TGA)	3291	2682	42	120
Coconut Char (Packed Bed)	3558	3521	35	129
Wyodak Coal Char (TGA)	681	1286	43	109

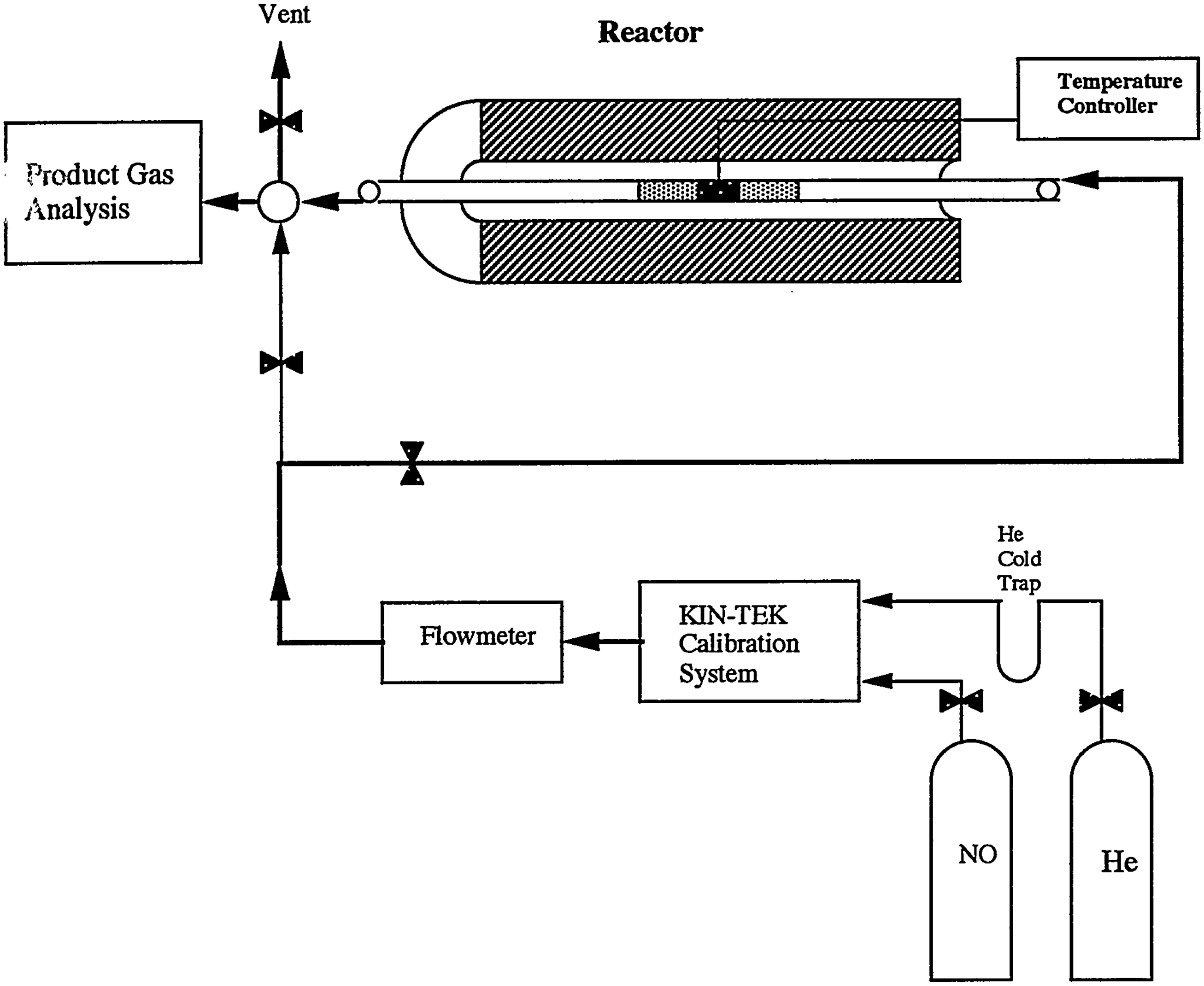

Figure 1. Schematic of packed bed reactor system.

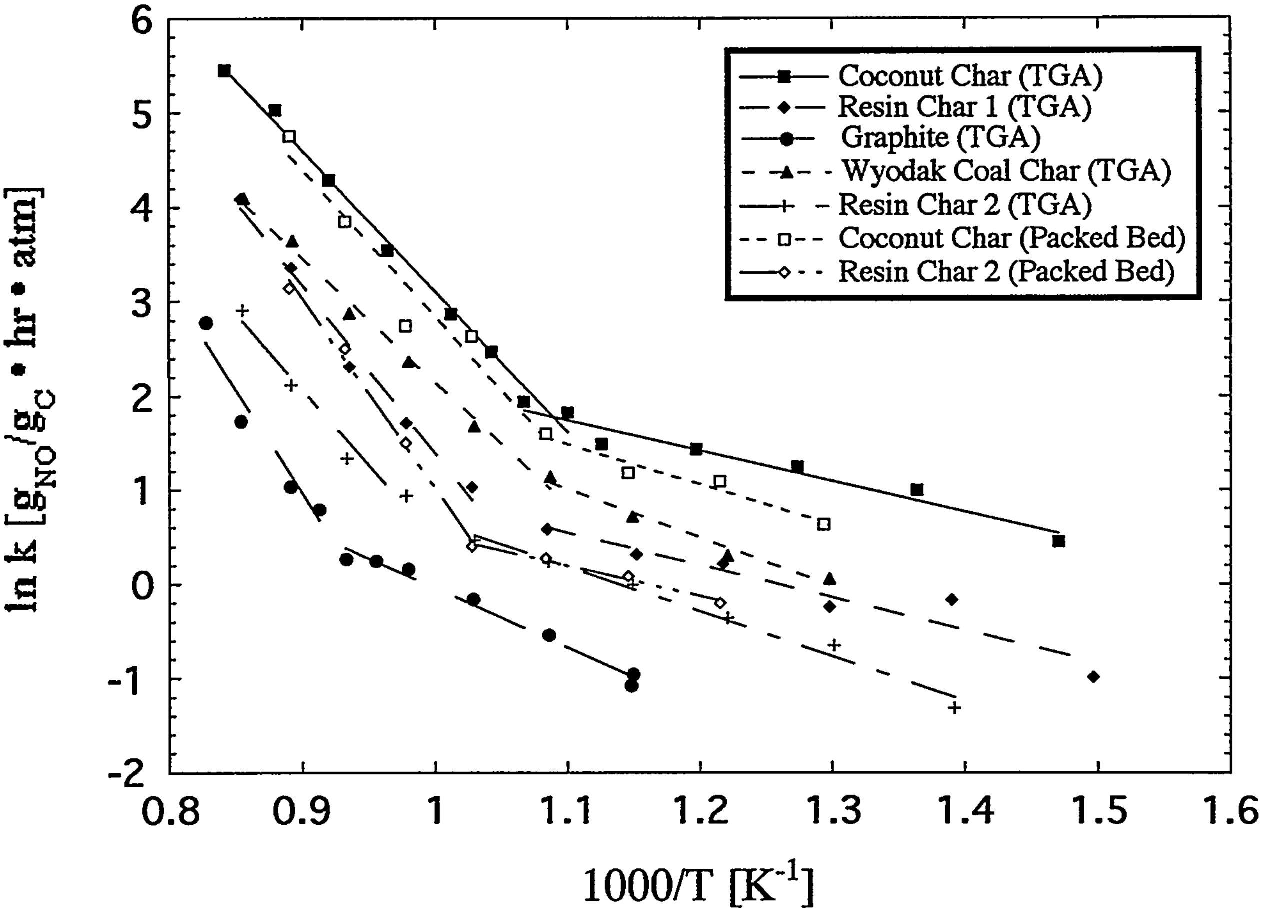

Figure 2. NO-carbon reaction rate constant, per unit mass of carbon reactant.

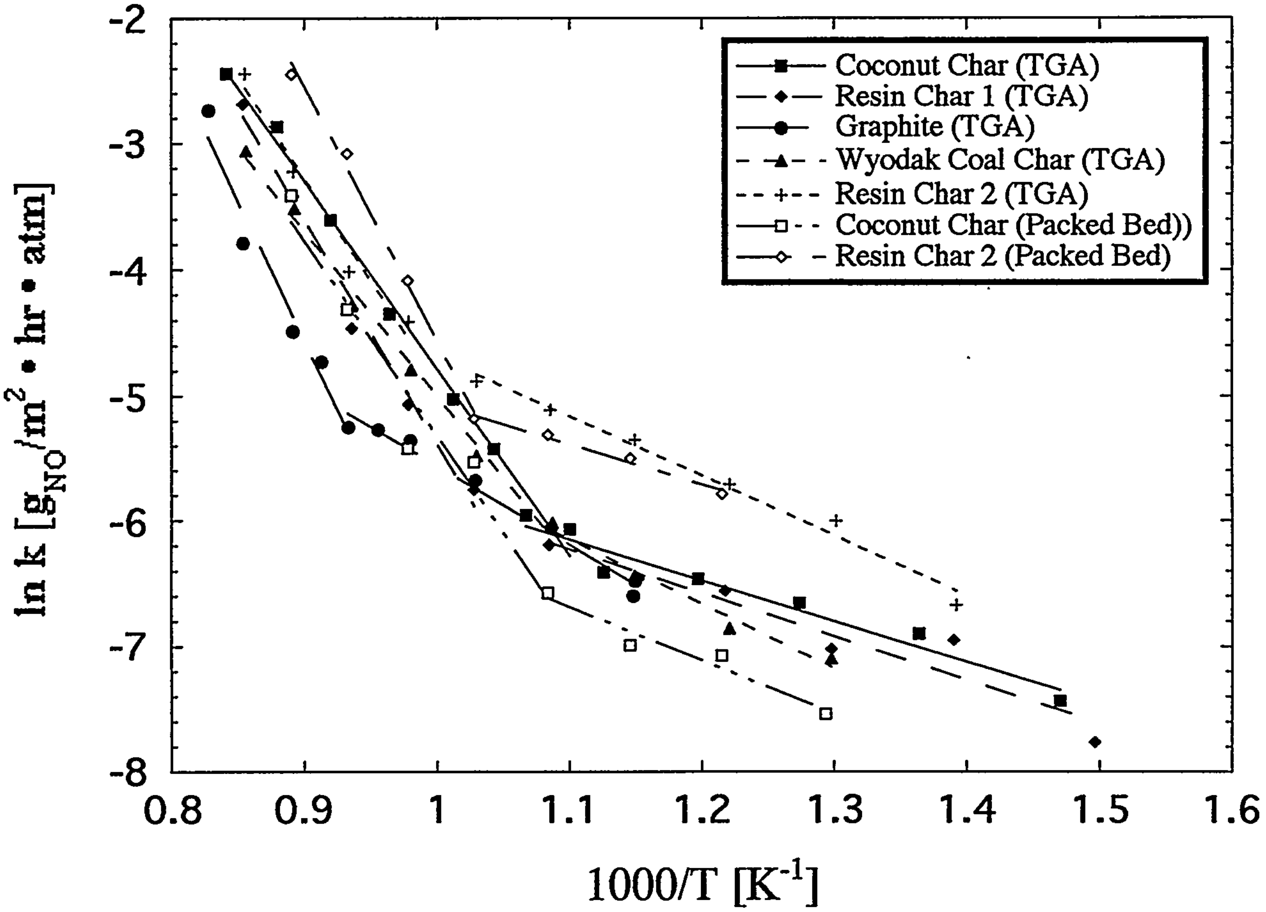

Figure 3. NO-carbon reaction rate constant expressed on a surface area basis.