

A COMPARISON OF THE REACTIVITIES OF DIFFERENT CARBONS FOR NITRIC OXIDE REDUCTION

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INTRODUCTION

Carbon has been recognized to play a significant role in reducing NO in some combustion systems (e.g., fluidized beds) and offers the potential as a reducing agent in other, new applications. In order to more fully appreciate this potential, it is useful to explore what factors influence the reactivity of carbons (and, more generally, chars) towards NO. This paper summarizes what is known about the reactivity of different carbons, and examines some questions raised by the comparison, in light of new experimental results.

The reduction of NO by carbons may, for simplicity, be represented by the general reaction:



Other products (for example, N₂O) are possible under certain specific conditions. Likewise, other reaction pathways (involving carbon catalyzed NO reduction by CO) are also possible. Still, the main carbon reduction route involves the products as indicated. Many aspects of this reaction system have been reviewed in recent years [e.g., 1-4]. Many of the published data on the NO-carbon reaction are summarized in Figures 1 and 2. A more complete summary of the available data is in preparation, and will be presented shortly. This summary is intended to convey the essential features of what is known about the kinetics of the reaction.

Figure 1 presents the data on the rate constant for the reaction, expressed as an NO consumption rate, on a per unit mass of carbon basis. The assumption has been made, consistent with most reports in the literature, that the reaction is first order with respect to NO [1, 2, 5- 8]. Several features are immediately apparent. First, there is a significant spread in the rates of reaction. The variation is of two to three orders of magnitude, which may not initially be surprising inasmuch as the data were not normalized based on surface areas, *vide infra*. It is apparent that there is quite commonly a shift in apparent activation energy of the rate constant. The "breaks" occur at temperatures ranging from about 900 to 1050 K, and always involve an increase in activation energy with increasing temperature. This break has been earlier noted by several groups. It must involve a change in mechanism, as opposed to an encroachment of heat and/or mass transfer effects, since the shift is in the direction of higher activation energies with increasing temperature. A hypothesis to explain the two regimes has been previously advanced [2]. The individual studies offer a wide range of activation energies, with some sets showing no evidence of the "break". There are surprisingly few clear trends with the nature of the carbon. For example, a highly pyrolyzed resin char exhibits a lower reactivity than does a graphite. De-ashing of a lignite char shows only a modest effect on reactivity. A cellulose char with low inorganic impurity content is seen to have a higher reactivity than coal chars.

Figure 2 presents a comparison of literature data on a surface area-normalized basis. The surface areas were taken as reported by the investigators themselves, and include some measured by nitrogen sorption and others with carbon dioxide. It should be noted that the data sets represented in Figures 1 and 2 are not identical, because the data were not always available to include results on both plots. It is perhaps surprising that converting data to a surface area basis does little to reduce the amount of scatter in the data. It is worth noting that the degree of scatter is not unlike that observed in similar summary plots of data on the oxygen-carbon reaction [9]. Thus it appears as though there is a high degree of variability of carbon reactivity towards NO, just as there is towards oxygen. This has been attributed to differences in the numbers of active sites per unit surface area. It is not yet possible to predict this value. It is interesting to note that the graphites exhibit relatively high reactivities per unit surface area. There is, however, no clear trend in reactivity with the nature of the carbon.

The results of Figures 1 and 2 present a confusing picture of the factors that influence the reactivity of carbons towards NO. While small subsets of the data can be compared and logical hypotheses drawn regarding the influence of certain variables, there is not yet an ability to predict reactivity to better than orders of magnitude uncertainty. The problem with an approach based upon comparing reactivities from literature accounts is that there are a number of experimental variables that may have had an influence on reactivity, and these are never completely controlled or reported. Most of these variables have to do with how the carbon is prepared, but some might also have to do with how the reactivities were determined. The remainder of this paper will explore how measured reactivities can be influenced by a number of experimental factors.

EXPERIMENTAL

Two different reactor systems were selected for study, in order to represent the two most widely employed techniques for study of this reaction. The first reactor system was a thermogravimetric

analyzer (TGA). In this case, a TA Instruments TGA was employed. As compared with the Cahn TGA system in which we had performed most of our earlier work [1,2], the TA Instruments TGA has a somewhat smaller enclosed gas volume. Thus, the experiments were performed with a continuous gas flow through the TGA to ensure that depletion of NO was not significant. The TGA work was performed, as earlier [1,2], at quite high NO partial pressures, ranging from about 1 to 10 kPa of NO partial pressure.

Many of the studies reported in the literature have employed packed bed reactors. One of the advantages of these systems is that they more realistically simulate possible "end-of-pipe" reduction systems. They also tend to be less complicated to operate, allowing for a steady flow of NO-containing gas which is continuously analyzed using an NO_x analyzer. Operation at lower, more realistic, NO concentrations is also possible. Operation of a TGA at low NO concentrations is often considered impractical, because of the long times needed to achieve significant burnoff (weight loss).

In our case, we employed a 4 mm ID packed tubular reactor, made of quartz. A bed of between 20 and 200 mg of carbon (char) was packed into a predetermined length of between 1 and 30 mm, depending upon the conditions to be studied. The bed was held in place with quartz wool. Blank runs indicated no significant NO reduction in the absence of carbon (this was not the case if ordinary glass wool was employed). A carrier flowrate between 70 and 125 cc/min of helium was passed through the reactor. In the work considered here, the only other component in the inlet gas was NO. The inlet NO concentration ranged between 100 and 300 ppm. The particle size in the bed was approximately 200 μm in all cases. Before all runs, the surface of the char was cleaned of oxides by heating at 1173 K for one to two hours.

RESULTS AND DISCUSSION

Several different carbons were tested in the TGA, using a consistent protocol. The samples examined were a resin char (ex-phenolformaldehyde) that we had earlier extensively studied [1,2], a graphite powder (from AESAR/Johnson Matthey Company), a coconut char (from Fisher Scientific), and a Wyodak coal char, prepared from a sample obtained from the Argonne Premium Coal Sample Program. The results are shown in Figure 3.

The results of Figure 3 show that this wide range of carbons gives fairly consistent rates, when the results are represented on a unit surface area basis. The one exception is the rates from our earlier work [1,2], and the reasons for this will be discussed below. It should be noted that the carbons range from those of quite high purity (the phenolic resin char and the graphite) to a mineral-containing coal char. The good agreement between the carbons and chars might be attributable to the fact that an effort was made to compare highly heat treated materials, in this case. The coconut char and graphite were used as-received (apart from surface cleaning at 1273 K for one hour). The phenolic resin char and the Wyodak char were prepared by a two-hour pyrolysis at 1223 K, and then surface cleaned prior to use. Thus for carbons and chars which may be considered as "old" there is quite good agreement in reactivity. Further tests, which will be reported separately, have not surprisingly indicated that the "age" of a char (i.e., how severely it is heat treated) does indeed have some effect on its reactivity. Here, however, it came as a surprise that the aging seems to lead to similar reactivities towards pure NO, despite significant differences in contents of impurities.

Figure 3 also indicates that the "break" in the Arrhenius plots depends upon the type of carbon. It can be seen that the break occurs at a much higher temperature in the graphite than in the other carbons. The agreement between the reactivities of the different carbons, on a per unit mass basis, was not nearly as good. In fact, the results gave a spread similar to that seen in Figure 1. Thus it appears that the reactions occur in Zone 1, and that the micropore area of the carbons is significant.

When our earlier TGA results on the same resin char are compared with those from the present study, there appears to be a significant difference (see Figure 3). This turned out to be a consequence of how the sample was prepared, and indicates an important consideration in developing experimental testing procedures. The extent to which the resin char surface was cleaned of oxides was responsible for the differences in the observed rates. In our earlier work [1,2], the reactivity of the resin char was established as a function of temperature, merely by varying temperature and recording what appeared to be pseudo-constant rates. This might be considered a "normal" experimental procedure. In this more recent work, it was learned that by cleaning the surface of oxides, by heating at 1273 K for an hour between each temperature to be studied, the resulting pseudo-steady mass loss rate was significantly higher. This means that the oxide population on the char surface is a function of the reaction history of the sample, and that this, in turn, influences the observed rate. What may appear to be a pseudo-steady state rate might actually be slowly evolving, as the oxide population readjusts on a timescale longer than that used to obtain the rate. We had actually noted the same problem earlier, in connection with determination of the reaction order with respect to NO [1]. Failure to clean the surface between different partial pressures gave an apparently less than unit order with respect to NO, since the surface oxide population could only very slowly adjust to the new NO partial pressure. Thus it is essential to report how kinetic experiments are performed, in order to establish a sample reaction history. Without this information, comparison of rate data from the literature may be quite misleading. Once this aspect of the process was noted, all our experiments were performed on a self-consistent basis, with surface oxide cleaning between each temperature step. Because we are measuring rates

on a virgin surface in each case, issues related to the influence of remaining oxides on rate are minimized. Further experiments in the TGA again established that the reaction is unequivocally first order with respect to NO partial pressure, validating the form of the rate constant used in Figures 1 through 3 (see Figure 4).

Generally, good agreement was obtained between the rate constants from the TGA and packed bed experiments, despite the fact that there was about a two order of magnitude difference in the concentrations of NO in the two reactor systems (around 2% in the TGA vs. 200 ppm in the packed bed reactor). Results for the coconut char in Figure 5, illustrate this conclusion. Further discussion of the small differences will be presented elsewhere. Thus apparently large differences in reactivity in Figures 1 and 2 are not attributable to what type of reactor system is used for testing, nor to the concentration level of NO employed. It is clear that the purity of the gas feed is important in determining the apparent reactivity; small amounts of oxygen affect rates significantly. This will be reported on elsewhere. We have further established, consistent with an earlier presented hypothesis [10], that it is difficult to obtain reliable reaction order information from packed bed experiments. This will also be reported elsewhere.

ACKNOWLEDGEMENT

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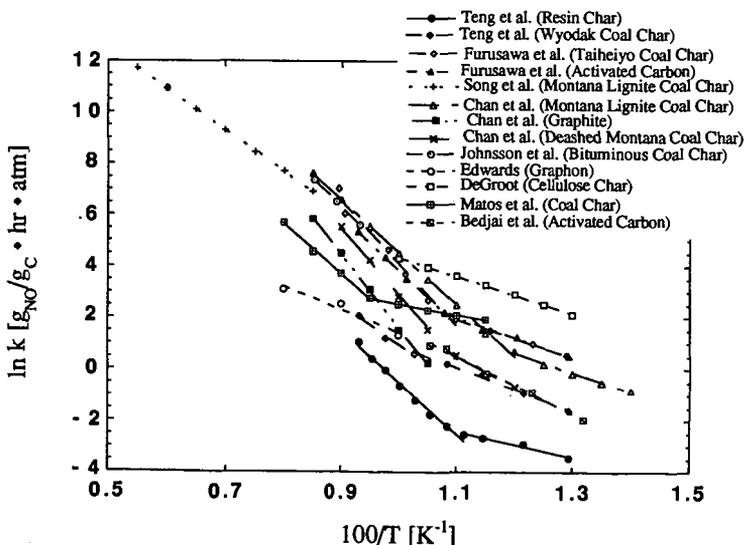


Figure 1. NO-carbon reaction rate constant, per unit mass of carbon reactant.

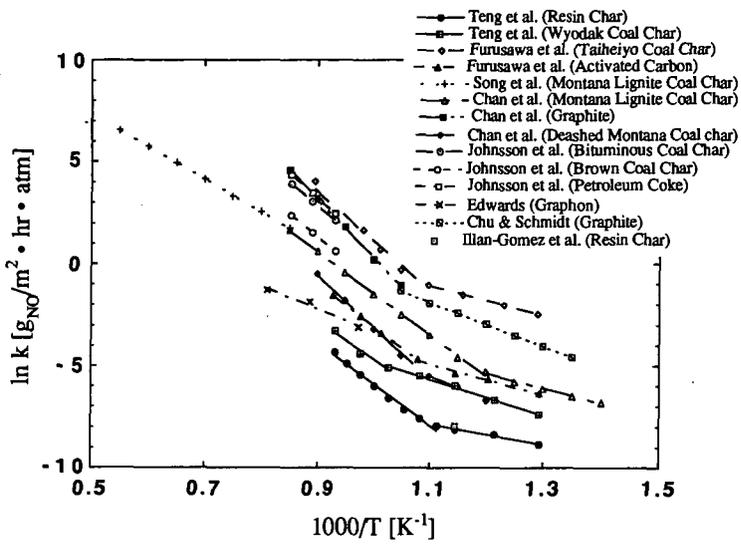


Figure 2. NO-carbon reaction rate constant expressed on a surface area basis

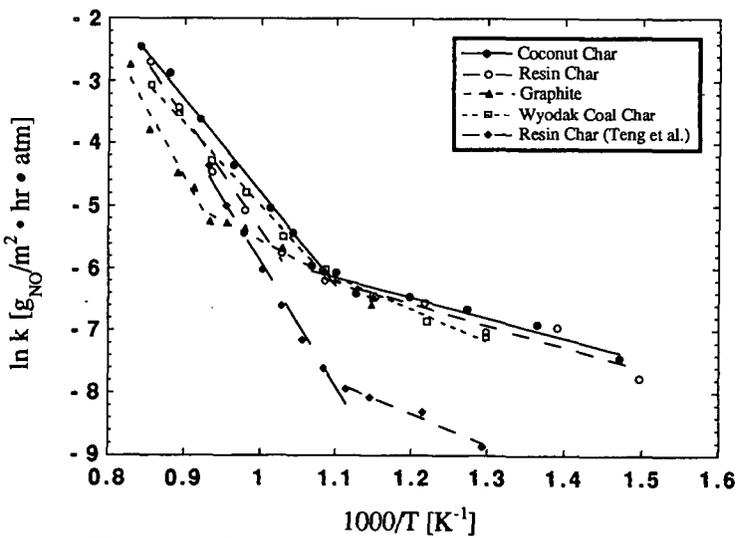


Figure 3. NO-carbon reaction rates from TGA experiments.

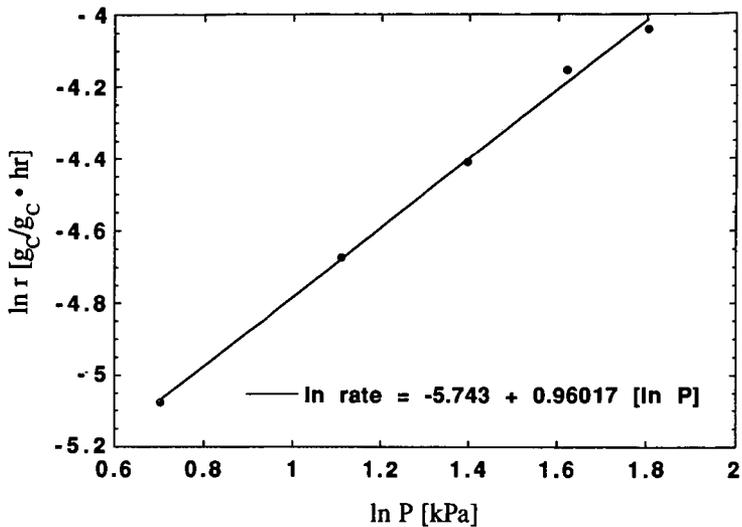


Figure 4. Reaction rate of resin char in the TGA, showing first order rate. ($T=600^\circ\text{C}$)

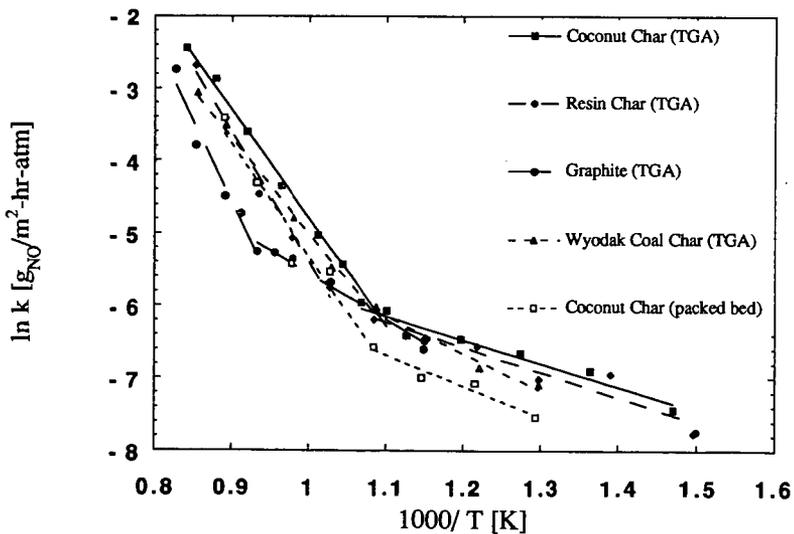


Figure 5. Comparison of rates obtained on various samples, in the TGA and packed bed reactor.