EFFECTS OF CO, CO2 AND O2 ON THE REACTIVITY OF NO WITH CARBONS

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Introduction

The reactions of NO with carbons are of interest in a number of practical devices. The interest here is in the high temperature reduction of NO by carbons. The kinetics of these reactions have recently been reviewed [1]. It has been noted over the years that other gas species may significantly affect the observed kinetics.

It has been suggested that the CO which is produced as a product of NO reduction on carbons may actually serve as a reactant for further reduction of NO, in suitable arrangements of the reaction system [1,2]. It has also been reported that oxygen can catalyze the reaction of NO with carbon, under certain circumstances [1,3,4]. It has normally been believed that CO_2 plays no role in the NO/carbon chemistry. The role of all three gases will be reconsidered in view of new experimental data.

Experimental

The kinetics of the NO/carbon reaction were examined in a packed bed reactor. The reactor consisted of a 4 mm ID, 500 mm long quartz tube, packed in its center with 20-500 mg of carbon particles, typically of a few hundred micrometer diameter. The bed was kept in place by quartz wool plugs. The reactor was heated in an electrical tube furnace. Blank runs verified that the quartz tube and wool did not influence observed kinetics. The reduction of NO was tracked by measuring the concentration of NO using a chemiluminescence analyzer (which also was used to verify the absence of NO_2 in the products). Appropriate concentrations of reactants were fed to the tube by controlled flow techniques.

Results and Discussion

The Influence of CO on NO Reduction

In the NO/carbon reaction literature, there exist a few reports of fractional order with respect to NO, which contradict the majority of results which show first order. It has bee recently hypothesized that this is an artifact of the contribution of the NO/CO reaction to NO reduction [1,2]. We have noted that generally, the reports of fractional order come from packed bed studies in which the carbon is fairly

reactive, and creates a high CO concentration through the primary reaction itself. The results of experiments in which we attempted to overwhelm the self-generated CO concentration by adding 400 ppm of CO to the feed are shown in Figure 1. The typical two-regime reaction behavior is seen in the absence of the added CO [1]. The CO is seen to significantly enhance the apparent rate of reduction of NO.

Figure 1. The effect of CO on NO reduction by Wyodak coal char. Circles- pure NO; squares- NO with CO added in feed
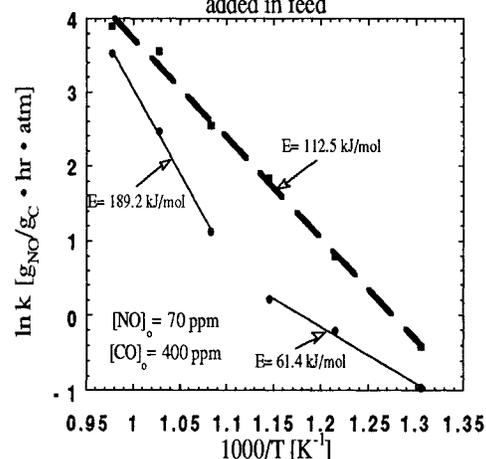
The kinetics of the carbon-catalyzed reduction of NO by CO may be estimated by subtracting the results for the reaction of NO with pure carbon from the results with added CO. The surface areas of the samples were the same. The influence of the product CO, in the case of the nominally pure NO reaction, is neglected, because the CO levels in that case are an order of magnitude lower that the of the added CO. The results of the calculation are shown in Figure 2. This figure shows the NO/CO reaction to be characterized by an activation energy of about 132 kJ/mol. There is also a suggestion of a mass transfer limitation at the highest temperature of the experiments.

An attempt at modeling the kinetics of reduction of NO in the presence of CO was based upon assuming that the processes of NO attack on carbon and NO reduction by CO occurred independently and in parallel. The relevant expression is:

$$r = k_1 P_{NO}^n + k_2 P_{NO}^m P_{CO}^j$$

Figure 2. The kinetics of the NO/CO reduction on Wyodak coal char.
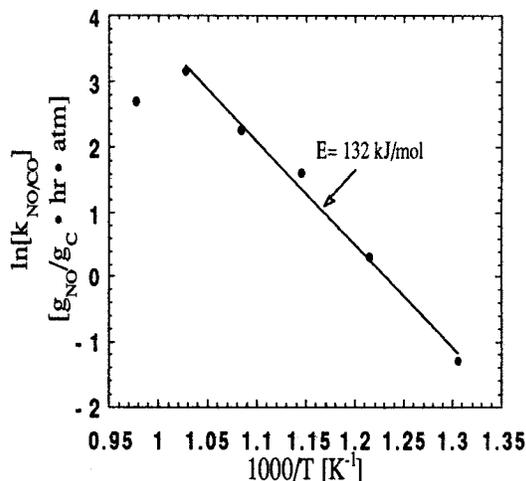

The activation energies for k_1 and k_2 are as given in Figures 1 and 2 (note that k_1 takes either of two values, depending upon regime). The value of n has been claimed to be near unity [1]. Based upon results with resin chars, we believe m is quite small, near 0.1. The value of j has been determined to be between 0.04 and 0.3. The value of m has been reported by another group to be fractional, and often quite small [5]. The order j has also been noted to be quite low, at low CO pressures [5].

The Influence of CO_2

It has often been assumed that CO_2 is essentially inert in the NO/C reaction system. It has, however, been found that there is often a measurable effect of added CO_2 on NO reaction rate, and that the effect involves inhibition of reduction.

Figure 3. The effect of CO_2 on NO reduction by graphite.
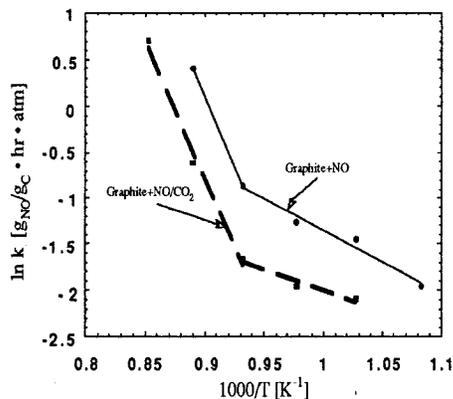
For example, Figure 3 shows the effect of CO_2 on reduction of NO by graphite. The NO concentration in this case is in the range from 60 to 100 ppm, and the CO_2 is 2%. With other carbons (coal chars), the inhibition effect is less pronounced at these low CO_2 concentrations, but it is still observable and is significant at CO_2 concentrations over 90% at atmospheric pressure.

The Influence of O_2

Oxygen is known to catalyze the reduction of NO by carbons [1,3,4]. Figure 4 illustrates the very complicated effects observed with graphite. The closed points are for pure NO and the open points for the case of added oxygen. Oxygen catalyzes reaction at some temperatures, inhibits at others, and opens up a third pathway at low temperatures. Thus studies of oxygen effects must take careful account of the temperature regime. Oxygen may be catalytic in some and inhibitory in others. The mechanism of the different effects are still unclear, though there is some support for the formation of active sites by oxygen attack.

Figure 4. The effect of O_2 on NO reduction by graphite.
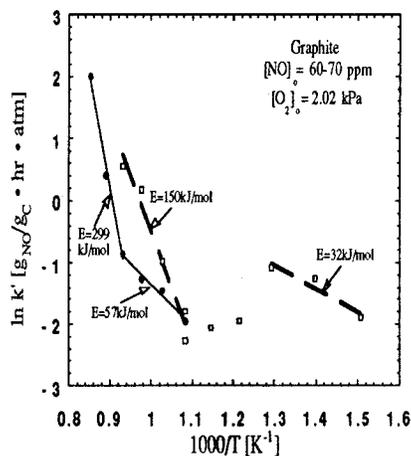
Acknowledgment

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