

THE KINETICS AND MECHANISM OF THE NO-CARBON REACTION: EFFECTS OF OXIDE GASES

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Introduction

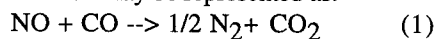
The role of other oxide gases on the rate of NO reduction by carbons has received attention in a number of studies. The earlier literature has been reviewed [1]. The role of CO has been hypothesized to influence experimental determinations of the apparent order of the reaction with respect to NO. Other aspects of this issue have been recently explored in another study [2]. Other oxidizing gases which may be expected to be present in a combustion environment can also significantly affect the rates. Some recent results related to this issue are presented here.

Experimental

Reaction rate measurements were performed in a packed bed reactor system, described in more detail elsewhere [3]. Briefly, it consisted of a 4 mm ID quartz reactor tube, packed with up to several hundred mg of fine particulate sample. This provided a bed length of 1 to 30 mm. Helium was flowed through the reactor at a rate of between 70 and 120 cc/min. NO reduction was used to determine kinetics. The NO reduction was monitored using a chemiluminescence analyzer. Several carbons were selected for study. Wyodak coal char samples and phenolic resin-derived samples were prepared by pyrolysis in inert gas at 1173 K for two hours. Another sample was polycrystalline graphite. Nitrogen isotherms and specific surface areas were determined in an automated volumetric gas adsorption apparatus at 77 K.

Results and Discussion

The surface-catalyzed reaction of CO with NO represents a separate, parallel reaction channel for destruction of NO in many carbon-NO reaction systems. It is important to separate out this reaction from the heterogeneous non-catalytic pathway, in order to develop a more complete kinetic understanding of the process. The surface-catalyzed reaction may be represented as:



A very large variety of surfaces have been reported to catalyze this reaction, including carbon. The kinetics of

this reaction have never been separately determined, however. These kinetics have been explored in this study, using experiments under identical conditions which involve reaction of NO over carbon, in the presence and absence of CO.

Figures 1 through 3 show the results of experiments conducted on three different carbons, Wyodak coal char, graphite and a phenolic resin-derived char.

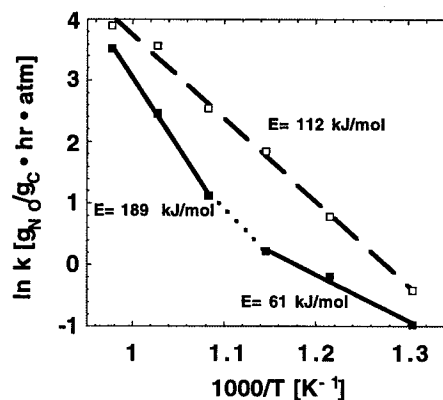


Figure 1. Reaction rate constants for reaction of NO over Wyodak coal char. NO concentration was 70 ppm in all cases. Solid points are for NO reduction by carbon alone, the open points are for the reduction in the presence of 400 ppm CO in the feed.

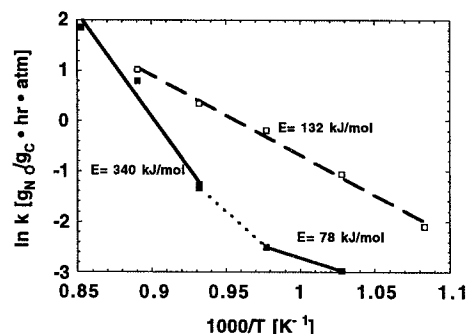


Figure 2. Same experiments as Fig. 1, but for graphite. The NO concentration was 65 ppm, CO 276 ppm.

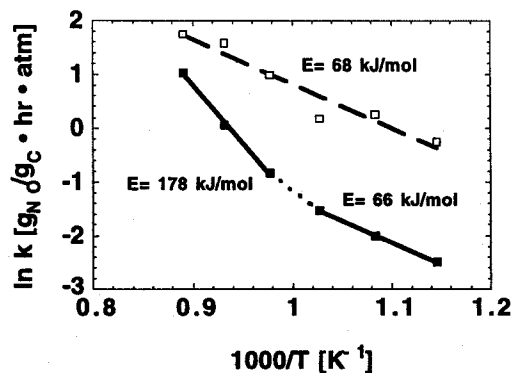


Figure 3. Same experiments as in Fig. 1, but for phenolic resin char. The NO concentration was 65 ppm, CO 270 ppm.

It is clear from the above three figures that there is a significant enhancement of NO reduction by CO in all of these cases. Since the carbons range from one which contains an abundance of potentially catalytic inorganic material (Wyodak char) to those that contain very little (both the graphite and the phenolic resin char), the enhancement is clearly associated with the role of carbon. Using these data, it is possible to estimate the extent of enhancement of the reaction by CO. The difference in the NO reaction rates with and without CO permits a separate accounting for the contribution of reaction (1). These calculations show that the activation energy of the part of the reduction process attributable to CO is 141 kJ/mol in the case of graphite and 132 kJ/mol in the case of Wyodak coal char. In the case of the resin char, a considerably lower value of activation energy is obtained, 54 kJ/mol. We attribute this lower value to the role of mass transfer limitations. In the case of the graphite sample, a companion paper in this symposium illustrates the surface area present in this material is all located in accessible porosity (mainly mesoporosity). In that same study, it was noted that the principal locus of reaction in the case of the Wyodak char is similarly sized porosity. Presumably, in these cases the CO will have access to the same pores as are used in the NO reaction.

The behavior of the resin char is somewhat different. Its pore size distributions are also somewhat different. The porosity of this char is dominated by micropores, and the development of porosity occurs mainly in that range of pore sizes. The absolute amount of meso- and macroporosity is also much smaller in the resin char than in the Wyodak coal char. Thus it is hypothesized that

the reason that the resin char is different than the other chars is that access to its internal surface is somewhat more limited.

In contrast to the observed effect of CO on NO-carbon kinetics, the effect of carbon dioxide is to retard reaction. Figure 4 shows the kinetics of NO reduction over the graphite sample in the presence and absence of added CO₂.

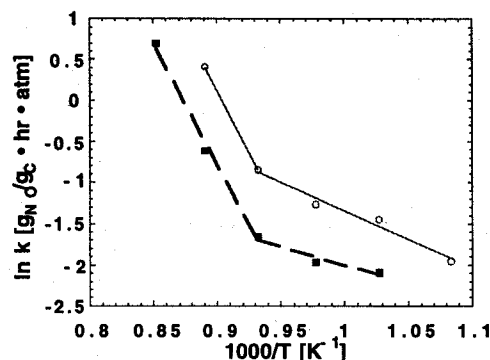


Figure 4. Reaction rate constants for reaction of NO over graphite. NO concentration was 80-100 ppm in all cases. The open points are for NO reduction by carbon alone, the solid points are for the reduction in the presence of 2.02 kPa of CO₂ in the feed.

The results for added CO₂ have been similar in trend for all of the carbons studied. There have, however, been large quantitative differences. For example, the effect of the same partial pressure of CO₂ on reduction of NO by Wyodak char is negligible. On the other hand, increasing the partial pressure to atmospheric gives a measurable decrease in rate. The effect of the lower partial pressure of CO₂ on the rate with resin char is likewise negligible. It is believed that the difference between the results for CO addition and for CO₂ addition has to do with the mechanisms of participation of the gases in the reaction system. The CO exhibits an effect at much lower concentrations because it has available a separate reaction channel, as is evident from the fact that reaction (1) is not specific to carbon surfaces. The CO₂ has no such NO reduction route available. Its main effect is to block surface sites with relatively refractory oxides.

References

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2. Aarna, I. and Suuberg, E.M., *27th Symp. (Int.) on Combustion*, 1998, p. 3061.
3. Aarna, I. and Suuberg, E.M. *ACS Div. Fuel Chem. Prepr.* 1996, 41, 284.