

THE NO-CARBON-REACTION: THE INFLUENCE OF CO AND POTASSIUM ON REACTIVITY AND POPULATIONS OF SURFACE COMPLEXES

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Introduction

A considerable amount of work has been conducted regarding the reactions of nitric oxide with carbon, due to the interest in this system as a means of reducing NO_x emissions, as well as in elucidating their role in heterogeneous combustion systems. It is also known that certain gases, such as NH₃, CO, and H₂, can act as reducing agents for NO in carbonaceous systems in which carbon behaves somewhat like a heterogeneous catalyst. Carbons can also be promoted with other active catalytic species. Thus, depending on the nature of the carbonaceous material and the operating conditions, carbon can behave like a reactant, a catalyst, and a catalyst support in this system. In the current work, the role of CO as a reducing agent and the effects of a catalyst (potassium) are explored. The results of this work also appear to have implications concerning the NO-carbon reaction in general.

Experimental

A quartz packed bed reactor/gas flow system was used for conducting the reactivity measurements, followed by thermal desorption. Gas concentrations up to of 500-4000 ppm of NO and CO in helium were used. A NO_x chemiluminescence analyzer and a quadrupole mass spectrometer were used for gas composition analyses.

Approximately 100 mg of phenol-formaldehyde resin char, produced from the same batch of resin and activated to 5% burn-off, was used for each run. Some of this material was loaded with potassium by immersion in potassium acetate (0.5M) at 60°C for 4h. The resultant char was washed with distilled water until no potassium was detected in the filtrate. The final potassium content of the char was determined by extraction in 1M HCl for 8h. Analysis by atomic absorption indicated a potassium content of 2.03% by weight.

The samples were thermally cleaned at 950°C for two hours prior to each run. They were then reacted isothermally in the selected gas mixture at a total pressure of one atmosphere to pseudo-steady-state conditions. At the end of the reaction run, the sample

was allowed to quench rapidly in helium by shutting off the furnace power and moving the furnace laterally off the packed bed. After cooling to 300K, temperature programmed desorption (TPD) of the surface complexes was performed at 20K/min in helium to approximately 1273K, while monitoring the gas phase composition with the mass spectrometer.

Results

Unpromoted Char. Steady-state reactivity experiments were performed at temperatures >923K. A summary of some of these data is presented in Figure 1. In this figure, the reactivities were normalized by the NO concentration. Thus, if the reaction were first order in NO, as has often been reported [1], these values would actually represent the first order rate constant. As shown in the figure, in the presence of just NO, the apparent activation energy is 180 ± 10 kJ/mol. In the presence of additional CO, however, the reactivity increased (by a factor of about 2-10, depending on temperature), and the apparent activation energy decreased to about 75 ± 8 kJ/mol. Moreover, the reactivity was insensitive to a variation of a factor of ten in the CO concentration (i.e., 50-500 ppm).

Sample CO evolution spectra following reaction in NO-He and NO/CO-He mixtures are presented in Figures 2 and 3, respectively. These spectra are obviously quite different from one another. As shown in Figure 2, the amount of evolved CO *increases* with reaction temperature, CO evolution occurs at high temperatures, and peaks are just about attained at the end of the heating regimen. A similar situation applies to the evolution of nitrogen, as shown in Figure 4. This is typical of what has previously been observed with just NO in the feed gas [1].

In Figure 3, the total CO evolution generally *decreases* with reaction temperature, and the CO evolution occurs at lower temperatures. Also, the total amount of CO evolved is greater than that in Figure 2. These spectra are actually more similar to those obtained following exposure of the thermally cleaned samples to just CO, as shown in Figure 6, for example. In the latter case, the

observed behavior of increasing CO evolution with decreasing exposure temperature is suggestive of a chemisorption equilibrium similar to what is observed in response to exposure of carbons to steam at lower temperatures, for example [2]. Thus, it appears that CO favors the formation of considerably more labile complexes than are formed during reaction in pure NO. On the other hand, the corresponding nitrogen TPDs for the NO/CO runs behave more similarly to those for just NO alone (see Figure 5). That is, the total amount of nitrogen-evolving surface complexes generally *increases* with reaction temperature and increasing NO concentration.

Under similar reaction conditions, it has been noted that the NO/CO reaction appears to exhibit close to zeroth order behavior with respect to CO [3]. This is also noted in the data in Figure 1. This suggests that a “stripping” reaction of the classic Eley-Rideal type:



where CO is oxidized by an oxygen surface complex to CO₂, and thereby acts to free active sites for subsequent NO attack, most probably cannot adequately explain the indirect catalytic effect of CO on NO reduction [3].

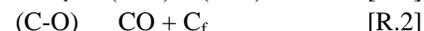
K-Promoted Char. As shown in Figure 1, in the presence of just NO, the effect of potassium-loading of the same phenolic char ranges from virtually none at high temperature (1123K) to about an order of magnitude greater at low temperatures (i.e., 923K) over that of the uncatalyzed char. This behavior is due to the substantial decrease in the apparent activation energy. However, the addition of significant amounts of CO in the feed gas does not appear to have any appreciable effect on the reactivity, unlike for the unpromoted char. Consequently, all the data in Figure 1 for the K-promoted char were fit to the same (gray) curve, which yields an apparent mean activation energy of about 100 ± 10 kJ/mol. This value is close to that for the CO-catalyzed reaction on the unpromoted char. Consequently, under these conditions, the “catalytic” effect of CO on NO reduction is much greater for the uncatalyzed char than is the effect of potassium in the promoted char. In addition, the catalytic effect of CO seems to be largely absent for the promoted char.

The TPD data for the K-promoted char are also different than for the unpromoted char. For example, nitrogen evolution appears to be significantly less at similar temperatures, and the trends in the CO spectra are non-monotonic. As an example, CO evolution spectra following steady-state reaction in 2000 ppm NO and 4000 ppm CO are presented in Figure 7. As shown, the CO evolution rate first increases with reaction

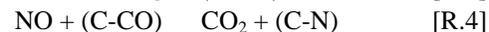
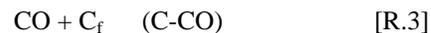
temperature, and then decreases again. This incorporates both of the qualitative behaviors observed for the unpromoted char in the absence and presence of CO, respectively.

Discussion

Unpromoted Char. For the pure phenol-formaldehyde char, the preceding results suggest a mechanism involving two different types of surface complexes - those formed by CO, and those formed by NO. The former are more labile (perhaps carbonyl-type complexes; C(s)-CO), and the latter are more strongly bonded (perhaps quinone-like structures; C(s)=O). For conditions under which there is little CO-generated complex available (e.g., reaction in NO/He at higher temperatures), NO can be directly reduced on “empty” active sites by dissociative chemisorption, and the oxidized carbon site can eventually desorb as CO:



It is noted, however, that CO₂ is the major oxidized carbon product species at lower temperatures for reaction in just NO. This is supported by the current CO adsorption results that show the population of the more labile complexes increasing markedly with decreasing temperature. This allows the relatively small amount of product CO from [R.2] to form a sufficient population of complexes that can then reduce NO to CO₂; e.g.,



in which the first step may act to saturate certain types of sites when sufficient CO is available in the gas phase. Thus, when the CO concentration is intentionally augmented by addition in the feed gas, the rate of the latter mechanism ([R.3] and [R.4]) can become comparable to that of the former ([R.1] and [R.2]). Consequently, the overall rate of NO reduction and the amount of CO vs. CO₂ product depend upon the rates of the two parallel processes. It is noted that the evolution of N₂ product remains the same in both cases; i.e., surface recombination of nitrogen complexes.

This proposed mechanism bears some resemblance to another mechanism proposed some time ago [4]. It explains the formation of both CO and CO₂ products, the so-called “two-regime” behavior that is observed for most carbons [1], and the behavior of apparent reaction order with respect to NO and CO. Consequently, it tends to unify various observations that have appeared in the literature.

K-Promoted Char. It is generally believed that the role of alkali metals in the NO-carbon reaction is to serve as a redox agent [5]. The metal is oxidized by NO and then reduced at its interface with carbon by “shuttling” oxygen to active carbon surface sites.

CO also provides a catalytic redox pathway *via* oxidation of a surface site that can subsequently reduce NO. Thus, in the case of the K-promoted char, all three NO reduction mechanisms may be present simultaneously; i.e., direct NO attack, reduction *via* CO, and the redox cycle on potassium. From Figure 1, under the current conditions it does not appear that reduction *via* CO competes very favorably with the redox cycle on potassium, although the rate of the latter is slightly lower. This might be due to the relative stability of the oxygen complexes formed; i.e., they may be more stable than those formed by CO. This is supported somewhat by TPD spectra such as in Figure 7 which show more stable complexes than in Figure 3, for example, at high and low temperatures, but it does not explain the formation of the relatively large amount of less stable complexes in the K-promoted char at 973K in Figure 7. In any case, as shown in Figure 1, as the temperature increases all the reactivity curves converge, suggesting that the rate of direct attack of NO on empty sites becomes the dominant reaction pathway at sufficiently high temperatures.

Conclusions

The relative reactivities of three NO reduction pathways on a particular carbon have been explored. Under the current experimental conditions it was found that catalytic reduction *via* CO can occur at a greater rate

than *via* the redox cycle on potassium, although the latter can predominate when both are present simultaneously. A general mechanism is proposed relating the catalytic effects of potassium and CO and the uncatalyzed direct attack of NO on active carbon sites. This mechanism bears some resemblance to one proposed by Smith *et al.* [4], and unifies various observations that have appeared in the literature.

References

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Acknowledgements

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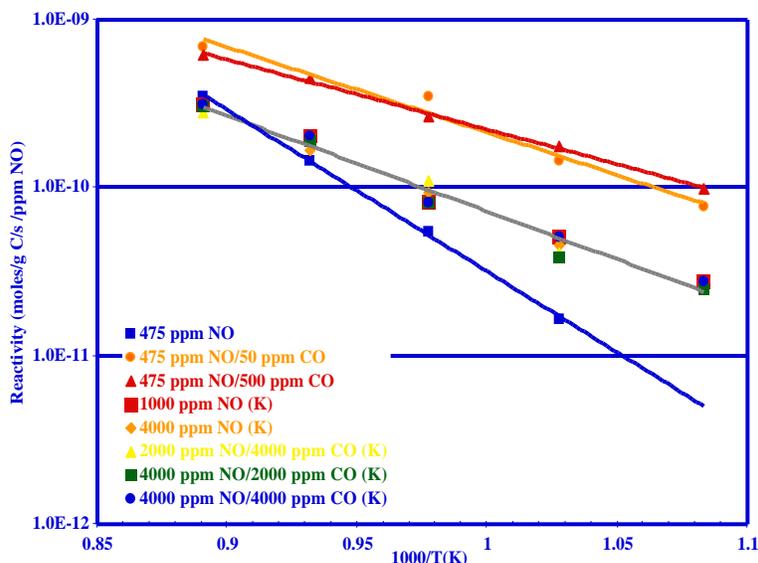


Figure 1. Reactivities of unpromoted and K-promoted phenolic resin char in NO/He and NO/CO/He mixtures.

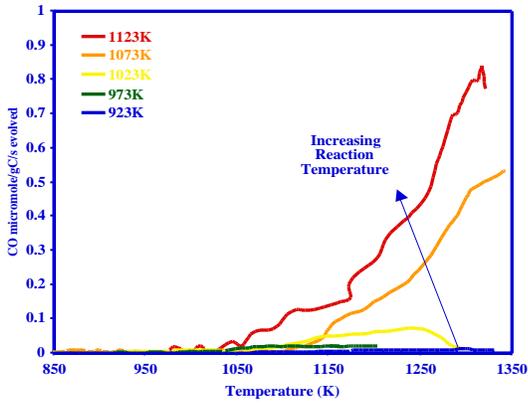


Figure 2. CO evolution rate at 20K/min following steady-state reaction in 475 ppm NO in helium as a function of reaction temperature.

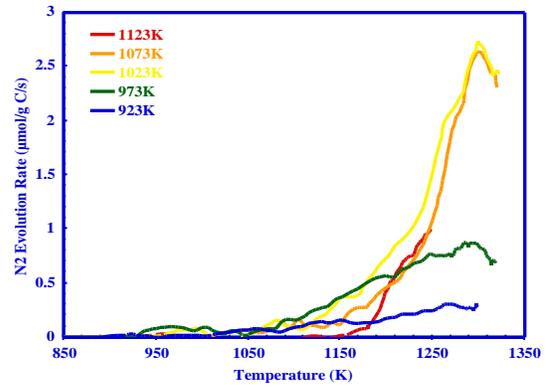


Figure 5. N₂ evolution rate at 20K/min following steady-state reaction in a 475 ppm/500 ppm NO/CO mixture in helium as a function of reaction temperature.

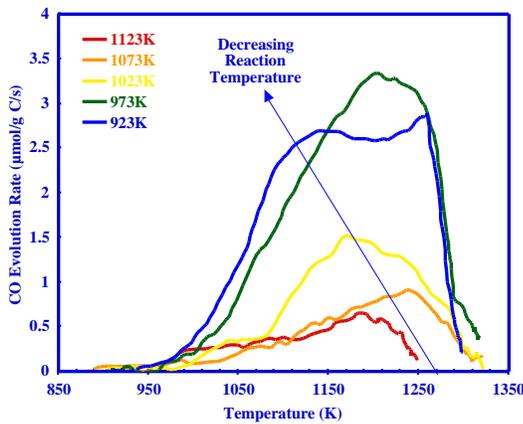


Figure 3. CO evolution rate at 20K/min following steady-state reaction in a 475 ppm/500 ppm NO/CO mixture in helium as a function of reaction temperature.

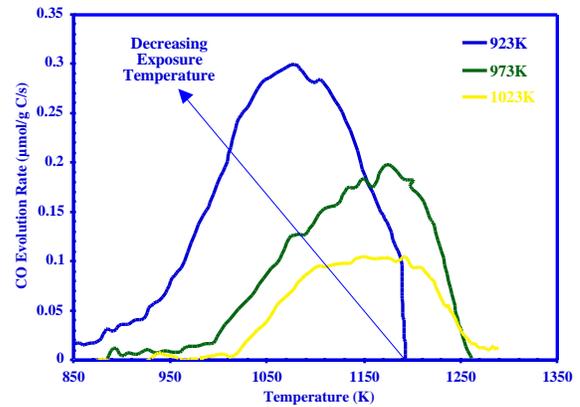


Figure 6. CO evolution rate at 20K/min following sample exposure to 50 ppm of CO in helium as a function of exposure temperature.

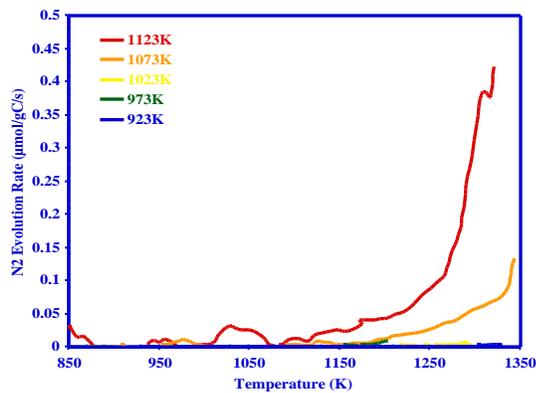


Figure 4. N₂ evolution rate at 20K/min following steady-state reaction in a 475 ppm NO in helium as a function of reaction temperature.

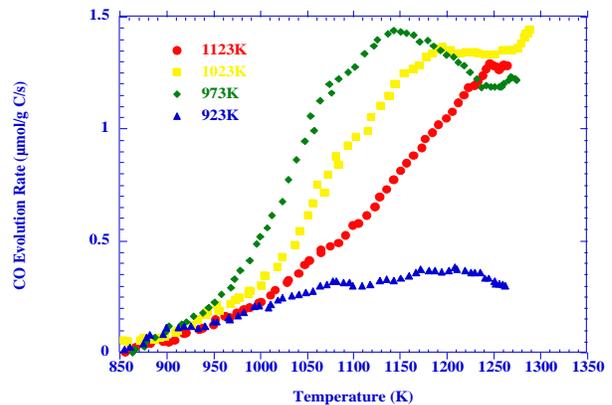


Figure 7. CO evolution rate at 20K/min following sample steady-state reaction in 2000 ppm NO/4000 ppm CO in helium as a function of reaction temperature.