TPR/TPD Studies of N_2O Decomposition on Carbons - Effects of Potassium and CO

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Abstract

N_2O reduction on a phenolic resin char and a coal-derived, demineralized char was investigated using temperature programmed reaction (TPR) and post-reaction temperature programmed desorption (TPD) techniques. The behavior of the samples was compared both with and without potassium (K)-promotion.

Introduction

N_2O, is an atmospheric "greenhouse" gas, and like NO, it can also be effectively reduced by carbon. Moreover, it can be produced under certain conditions during NO reduction over metal-catalyzed carbonaceous systems [1,2]. Studies of catalytic decomposition of N_2O have appeared in the literature in recent years. Catalysts that have been applied to heterogeneous N_2O decomposition include metals, such as Pt and Au, and pure and mixed oxides, supported on alumina, silica, and zeolites [3]. However, little information is available in the literature on N_2O conversion over carbon-supported catalysts, especially at low temperature. Activated carbons are common and useful catalytic support materials, as well as effective reducing agents [4].

N_2O has been reported as an intermediate in the NO-carbon reaction at lower temperatures [1,2,5]. Consequently, mechanisms of N_2O decomposition share some common features with NO reduction mechanisms on carbon. The heterogeneous reaction of N_2O with carbon can reduce N_2O to N_2 and form CO_2 and CO gaseous products. The overall stoichiometry is:

$$2N_2O + C \quad\quad CO_2 + 2N_2 \quad\quad\quad\quad\quad\quad (1)$$

$$N_2O + C \quad\quad CO + N_2 \quad\quad\quad\quad\quad\quad (2)$$

At low temperatures, the principal reaction products are N_2 and CO_2 [6-8], and the amount of CO increases with increasing temperature. However, some workers [9,10] have found only very low amounts of CO product gas.

The literature reveals conflicting conclusions regarding the effect of CO on the N_2O-carbon reaction. On the one hand it has been observed that the addition of CO generally enhances N_2O reduction [3,11-14]; while on the other hand Rodriguez-Mirasol *et al.* [6] concluded that CO has no direct effect on the reaction of N_2O with char, since N_2O itself can remove oxygen from the surface, thereby minimizing the importance of

oxygen removal by CO in the presence of significant amounts of N_2O. In this paper, the influences of CO and potassium on the N_2O-carbon reaction are explored.

Experimental

Reactivity measurements were conducted in a quartz, packed bed reactor/gas flow system. Two different types of experiments were carried out for the N_2O studies: (1) temperature programmed reaction (TPR), consisting of heating the sample at 20 K/min to 950°C in a mixture of 4000 ppm N_2O in helium; and (2) isothermal reaction between 200°C and 450°C in a mixture of 4000 ppm N_2O/4000 ppm CO. A quadrupole mass spectrometer (QMS) and a dual-column (Carbosphere and HayeSep columns) gas chromatograph were used for gas composition analyses.

Two different chars were examined in this work. One was prepared from phenol-formaldehyde resin (all from the same batch), and the other from Wyodak subbituminous coal samples obtained from the Penn State coal sample bank (DECS-26/PSOC-1566). Samples of the latter were also demineralized with a mixture of HCl/HF solutions. All the samples were pyrolyzed in a tube furnace at 1273K for 2h in a flow of high-purity helium. They were then activated in oxygen at 520°C; the resin char to approximately 6%, and the Wyodak char to about 10% burn-off. Some char samples were promoted with potassium by immersion in potassium acetate (0.5M) at 60°C for 4h. The resultant materials were 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 in the resin char, and 1.21% by weight in the demineralized Wyodak coal char.

Char 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 atmospheric pressure 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 rapidly 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.

Results and Discussion

Temperature Programmed Reaction (TPR). TPR results in 4000 ppm N_2O in He over potassium-promoted and unpromoted phenolic resin char at 20K/min are presented in Figures 1 and 2, respectively. As shown in Figure 1, N_2O reduction over the potassium-promoted resin char is facile, beginning at about 200°C. CO_2 production is much greater than that of CO at low temperatures, and it peaks at about 900°C.

In comparison, the data in Figure 2 indicate essentially no reaction over the unpromoted resin char until about 400°C. In addition, unlike in Figure 1, CO production is always greater than, or at least comparable to CO_2.

It is noted that the oxygen balance closes quite well in both figures. The *total oxygen* $(CO + 2CO_2)$ curve follows the N_2 evolution curve very closely. Thus all the oxygen in N_2O is accounted for. Consequently, the CO product gas is most probably due to direct desorption of previously accumulated C(O) complexes, as well as some contribution form CO_2 gasification at the higher temperatures.
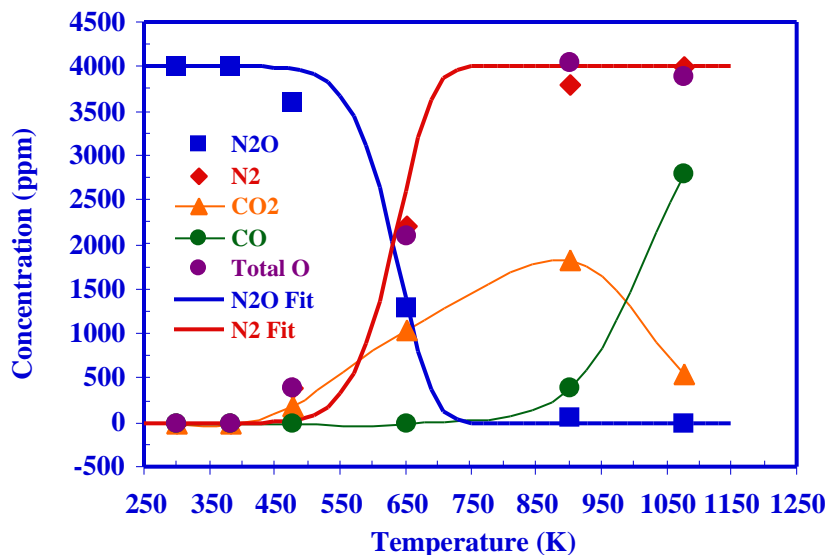

Figure 1. Species evolution during temperature programmed reaction (TPR) at 20K/min in 4000 ppm N_2O in helium over potassium-promoted phenolic resin char (K-PRC). The solid curves for N_2O and N_2, CO_2 and CO were calculated assuming first order behavior with E= 65 kJ/mol.
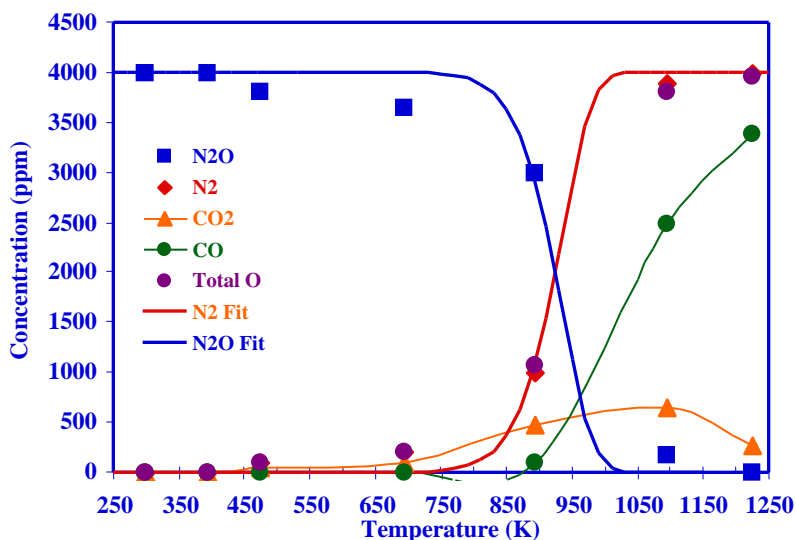

Figure 2. Species behavior during temperature programmed reaction (TPR) at 20K/min in 4000 ppm N_2O in helium over unpromoted phenolic resin char (PRC). The solid curves for N_2O, N_2, CO_2 and CO were calculated assuming first order behavior with E= 157.7 kJ/mol.

Thus, the catalytic effect of potassium is quite substantial for N_2O decomposition over the phenolic resin char, in terms of both decreasing the effective temperature range for the onset of reduction, as well as producing primarily CO_2 product at low temperatures.

The fit curves for N_2O consumption in Figure 1 were calculated assuming the experimentally-determined apparent reaction order and activation energy of n = 1 and E= 65 kJ/mol over the potassium-promoted resin char. For a first order reaction under conditions of a linear heating ramp of slope (K/min), the concentration of the reactant is given by [15]:

$$C_{N2O} = C_0 \exp[-(\nu_1 RT^2/\beta E) \exp(-E/RT)], \qquad (3)$$

where C is the reactant concentration as a function of reaction temperature, C_0 is the feed reactant concentration, ν_1 is the first order rate constant pre-exponential factor, R is the universal gas constant, E is the activation energy, and T is the absolute temperature. By stoichiometry, the concentrations of the products are:

$$C_{N2} = C_{Total\ O} = C_0 (1-\exp[-(\nu_1 RT^2/\beta E) \exp(-E/RT)]). \qquad (4)$$

The pre-exponential factor required to fit the experimental data in Figure 1 was 6.5×10^4 min^{-1}. As can be seen, the resultant fits with Eqns. (3) and (4) are quite reasonable.

The reaction order for the unpromoted resin char was determined to be close to *zeroth* order at 600°C. The expression for the reactant concentration undergoing a *zeroth* order reaction under a linear heating regimen is [15]:

$$C = C_0 - (\nu_0 RT^2/\beta E) \exp(-E/RT), \qquad (5)$$

where ν_0 is the corresponding zeroth order rate constant pre-exponential factor (e.g., ppm/min). However, Eq. (5) did not fit the N_2O data in Figure 2 very well, since it requires a sharp decrease to zero when the second term becomes equal to the initial concentration, rather than sigmoidal as indicated in the figure. The first order rate form (i.e., Eq. (3)) fits the data much better. Thus, the first order rate form was used with a representative activation energy of 157.7 kJ/mol from Smith *et al.* [7] to fit these data. The corresponding pre-exponential factor for the fit curve presented in Figure 2 was 2.5×10^8 min^{-1}. Of course, this is only a rough approximation, since the apparent activation energy and reaction order have been observed to vary significantly over this range [10], and the well-known kinetic "compensation effect" makes an infinite number of activation energy/pre-exponential factor combinations possible. In any case, these results suggest that the zeroth order behavior observed at 600°C does not seem to apply over the entire TPR temperature range. Zeroth order behavior for the unpromoted resin char most probably applies only under conditions where the oxygen surface complex coverage is high, and the overall reduction rate is desorption rate-controlled (*i.e.*, at the lowest temperatures). At high temperatures, where the overall rate becomes oxygen surface complex formation rate-controlled, the apparent order should be closer to unity.

In Figure 3 are summarized the results of representative TPR experiments for the potassium-promoted, resin and demineralized Wyodak coal chars. As shown, N_2O reduction over the two potassium-promoted chars begins at about 200°C. The potassium-promoted resin char exhibits *greater* reactivity at high temperatures and *higher* N_2 and CO_2 product yields than the K-promoted, demineralized Wyodak coal char. This behavior can be attributed to the greater amount of potassium present in the K-PRC char, as well as possibly better potassium dispersion in the resin char.
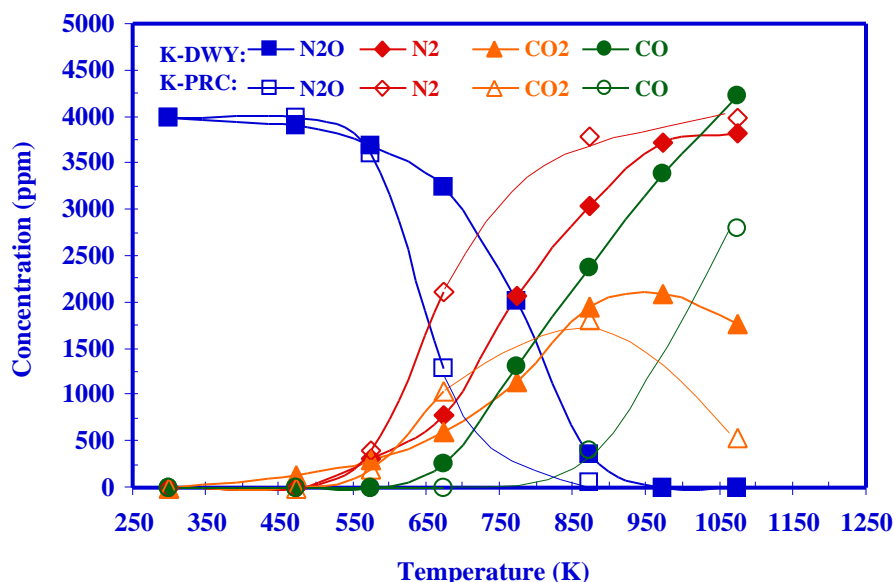

Figure 3. Species behavior during temperature programmed reaction (TPR) at 20K/min in 4000 ppm N_2O in helium over potassium-promoted demineralized Wyodak coal char (K-DWY) and resin char (K-PRC).

N_2O reduction over the potassium-promoted resin char produces primarily CO_2 and very little CO. However, considerably more CO is produced over the potassium-promoted demineralized Wyodak char. The latter could be due to the formation of more labile oxygen surface complexes on the K-DWY than the K-PRC that desorb at lower temperatures.

The Effect of Additional CO and TPD Spectra. A summary of the reactivities of the potassium-promoted resin char (K-PRC) and demineralized Wyodak coal char (K-DWY) samples with additional CO in the feed gas is presented in Figure 4. As shown, the K-DWY exhibits *greater* reactivity than the promoted resin char. This can be attributed to the effect of residual mineral matter in the demineralized Wyodak coal char. For the K-PRC, the additional CO in the feed gas has no observable effect on the N_2O reduction rate. A comparison of CO and CO_2 evolution data from potassium- promoted resin char following reaction at 400°C in 4000 ppm N_2O and in a 4000 ppm N_2O/4000 ppm CO mixture is presented in Figure 5. It is noted that although the CO_2 evolution remains essentially the same, the CO evolution is much *greater* in the case of additional CO in the feed gas. The fact that the CO_2 evolution remains unchanged is consistent with the fact that the N_2O reduction rate remains unchanged. The greater CO evolution

may be at least partially due to CO desorbed at lower temperatures, re-chemisorbing to produce higher temperatures complexes [16,17].
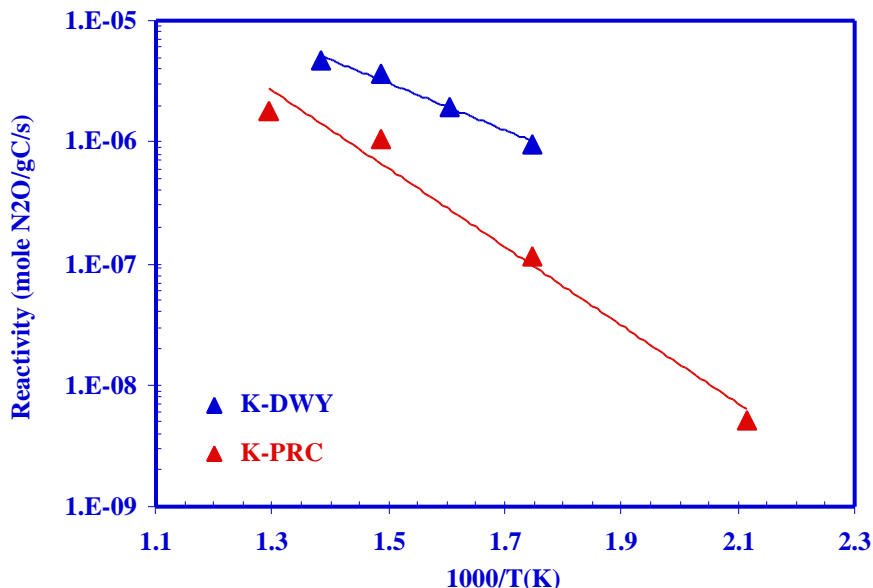

Figure 4. Summary of char reactivities in a 4000 ppm N_2O/4000 ppm CO mixture in the packed bed reactor.
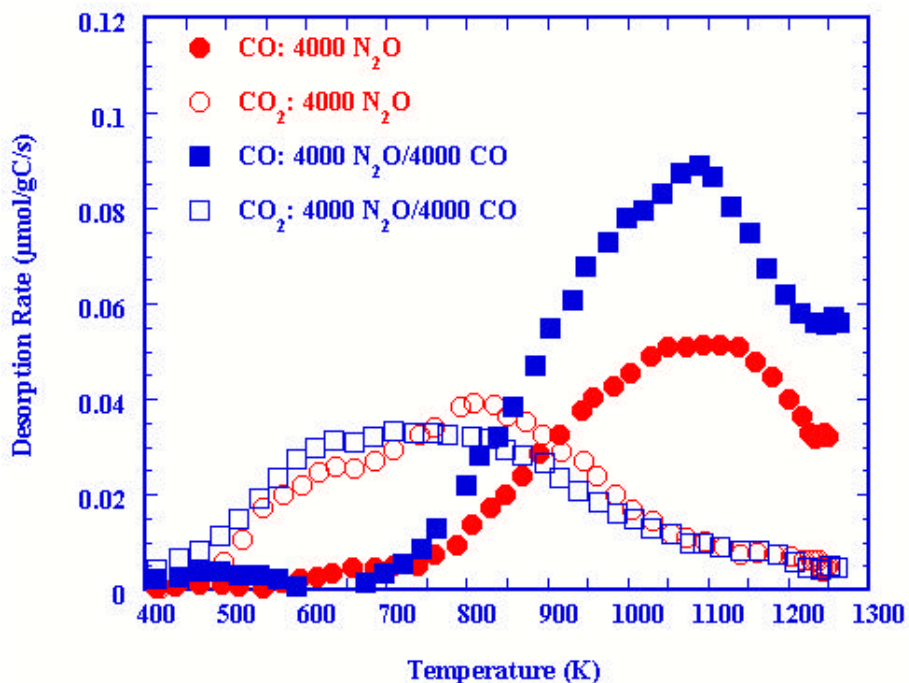

Figure 5. Comparison of CO and CO_2 evolution data at 20 K/min from potassium-promoted resin char following steady-state reaction at 400°C in 4000 ppm N_2O and in a 4000 ppm N_2O/4000 ppm CO mixture.

However, different results were obtained for the K-DWY char. For this char, the presence of additional CO in the feed gas increases the reactivity and decreases the apparent activation energy to about 37±1.7 kJ/mol. Moreover, the fractional conversion

of N_2O over this char at 400°C in 4000 ppm N_2O was 10%, while the addition of 4000 ppm CO to the feed gas increased the fractional conversion to 74%, while producing larger amounts of N_2 and CO_2. The effect of additional CO in the feed gas on the product gas distribution for this char is presented in Figure 6.
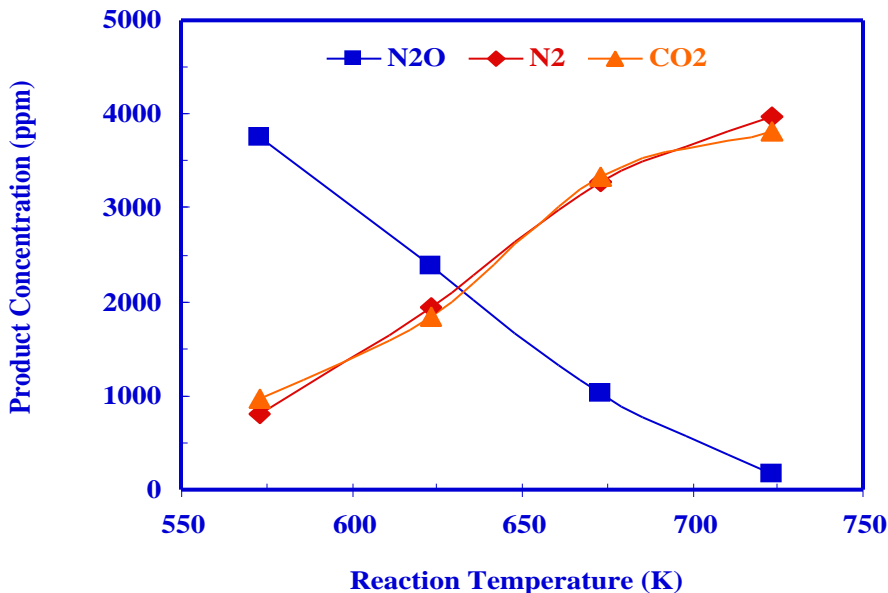

Figure 6. Steady-state product gas distribution as a function of reaction temperature in a 4000 ppm N_2O/4000 ppm CO mixture over K-promoted, demineralized, Wyodak coal char (K-DWY).
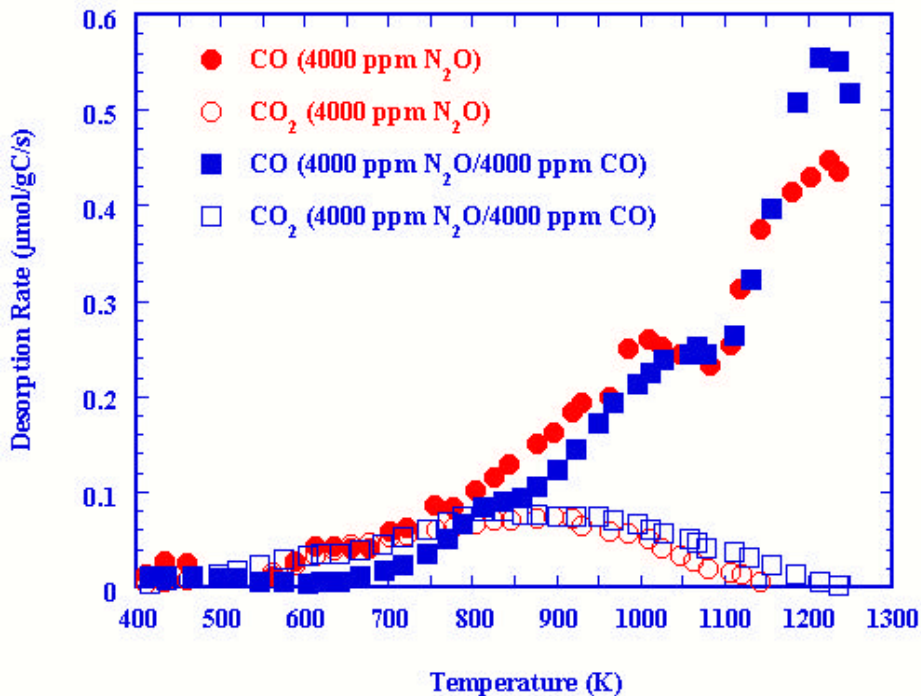

Figure 7. Comparison of CO and CO_2 evolution from potassium-promoted, demineralized Wyodak coal char following steady-state reaction at 400°C in 4000 ppm N_2O and in a 4000 ppm N_2O/4000 ppm CO mixture.

As shown, the amount of product CO_2 is about the same as that of N_2, which indicates that in the presence of additional CO, the reaction stoichiometry is:

$$N_2O + CO \quad CO_2 + N_2 \tag{6}$$

The additional CO increases the reactivity, presumably *via* the indirect reaction of CO with chemisorbed oxygen deposited by N_2O on the surface, creating a free site for further reaction with N_2O. However, the additional CO in the feed gas does not appear to affect the CO and CO_2 TPD spectra from the K-promoted, demineralized char, as presented in Figure 7. Therefore, it is assumed that the additional CO reacts with chemisorbed oxygen produced by N_2O decomposition on a catalytic active site from residual mineral matter impurities in the demineralized char, releasing CO_2 and creating a vacant active site for further reaction with N_2O:

$$N_2O + M \quad N_2 + M(O) \tag{7}$$
$$CO + M(O) \quad M + CO_2 \tag{8}$$

Conclusions

In the concentration regime investigated, the apparent reaction order for N_2O reduction is close to first order for both the potassium- promoted resin char (K-PRC) and the potassium-promoted, demineralized Wyodak coal char (K-DWY), and close to zeroth order for the unpromoted resin char at low temperatures. In the latter case, the apparent order seems to increase to unity at higher temperatures. This behavior is attributed to reaction rate control by surface oxygen complex formation, catalyzed by metallic sites in the promoted resin char, and surface oxygen complex desorption in the unpromoted resin char at low temperatures.

The K-PRC exhibits *greater* reactivity at high temperatures and *higher* N_2 and CO_2 product yields than the K-DWY coal char. This behavior can be attributed to the greater amount of potassium present in the K-PRC, as well as possibly better potassium dispersion in the resin char. The CO produced at higher temperatures, is attributed to a combination of desorption of C(O) complexes and CO_2 gasification at higher temperatures.

For the K-PRC, additional CO in the feed gas has no observable effect on the N_2O reduction rate. However, for the K-DWY coal char, the effect of additional CO was both to increase the reactivity as well as the evolution of N_2 and CO_2 product gases, presumably *via* reaction of CO with chemisorbed oxygen produced by N_2O decomposition on catalytic active sites in the residual mineral matter impurities.

Acknowledgements

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