ON THE KINETICS OF NO REDUCTION OVER CARBON

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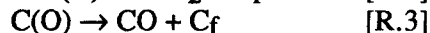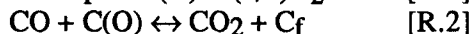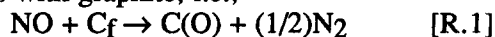Providence, Rhode Island 02912

Introduction

Interest in the use of carbons to reduce NO_x has resulted in a wide variation of reported "global" reaction orders, activation energies, and gaseous products distributions. Here we critically examine some of these issues to point out potential "pitfalls" concerning the interpretation of kinetic data for this reaction system.

The Model

The current analysis is focused on a packed bed reactor model of NO reduction on carbon, based on the kinetics of Chan et al. [1]. This model is intended to be only semi-quantitative in nature and is used simply to illustrate some important trends that are believed to be generally applicable to the NO-carbon system.

The model is based on the three-step kinetic mechanism proposed by Chan et al. [1] to explain their results with graphite; i.e.,

$$NO + C_f \rightarrow C(O) + (1/2)N_2 \qquad [R.1]$$
$$CO + C(O) \leftrightarrow CO_2 + C_f \qquad [R.2]$$
$$C(O) \rightarrow CO + C_f \qquad [R.3]$$

In order to account for CO production at higher temperatures, the back-reaction of [R.2] was also included. Its rate constant was estimated from the equilibrium constant of the oxygen exchange reaction as given by Strange and Walker [2]. This kinetic model was adapted to Montana lignite char, also used in the work of Chan et al. [1], by multiplicative scaling of the pre-exponentials of all three given rate constants to yield 37% NO conversion for the 873K experiment reported in Table 4 of their work (10 ml/s, 6700 ppm NO inlet concentration). This approach was used to account for the difference in active site concentrations between the two materials. The lignite char was only 30% as reactive as graphite on a per unit surface area basis.

A steady-state, plug flow model of the reactor used by Chan et al. [1] with the estimated volume for the sample mass (3.06 g) was formulated using these kinetic rate constants. The resultant gas composition profiles are shown in Figure 1. The model was tested by attempting to predict the 769K data in their Table 4. The result was 5% conversion, rather than 16%, as reported. Given the relative crudeness of the model, it was concluded that the comparison was reasonable. All the results presented here were determined using this model without any further modifications.

Results and Discussion

The results in Figure 1 show that the CO/CO_2 ratio varies over three orders of magnitude (i.e., from 17 to 0.1) from near the inlet to the outlet of the reactor. The effluent CO level predicted under these conditions is 112 ppm which is of the order required to close the oxygen balance in Table 4 of Chan et al. [1] (i.e., 181 ppm), although no CO concentration data are actually listed in that table.

From Figure 1, it is obvious that there are two different regimes of behavior of the CO/CO_2 ratio: i.e., early in the reactor where the two concentrations are comparable, and late in the reactor where the CO_2 concentration exceeds that of CO by a considerable amount. This behavior occurs because in the kinetic model the CO production and consumption reactions quickly reach a "steady-state" level near the inlet of the reactor, while the production of CO_2 continues to increase with NO conversion.

Exploration of the global kinetics of the NO-carbon reaction in the integral reactor was performed by varying both the feed NO concentration and the flow rate from 2.5 - 40 ml/s such that the molar flow rate of NO was constant at $6700 \times 10 =$ ppm ml/s (0.9 μmol/g s). This yielded a small positive apparent global reaction order of 0.065, with a corresponding activation energy of 176 kJ/mol between 773-873K. This latter value corresponds well to the 183 kJ/mol reported by the authors for the Montana lignite char in the low temperature regime [1]. However, the authors also determined the global reaction order to be unity. Not only was the global order determined here to be near zero, but it varied with flow rate such that for 0.625 - 10 ml/s it was 0.017 order, and for 10 - 160 ml/s it increased to 0.17 order. There are at least two possibilities for this apparent inconsistency. First, in the work of Chan et al. [1] the volumetric flow rate was varied only slightly less than a factor of four, so the sensitivity to order may not have been as great as here where the corresponding variation was two orders of magnitude. Another explanation may lie in the experimental technique and the history of the surface complex coverage of the samples. In order to test the consequences of either no or incomplete surface cleaning, the steady-state oxygen surface

coverage achieved during the nominal test run (i.e., 873K, 6700 ppm NO, 10 ml/s, 3.06 g char) was held constant, and the NO inlet concentration was varied. Indeed, as predicted by the kinetics [R.1], the resultant reaction order was unity. It is not known if the samples were cleaned of surface oxygen between runs in the actual experiments. Although the oxygen surface complex population eventually accommodates to changes in the inlet conditions, it does so relatively slowly, and this process will be even slower if the change is not very great, such that one may be easily fooled into thinking that steady-state has been attained, where in actuality it has not. Indeed, this problem was encountered in our own work [3], and ultimately we resorted to 2h of thermal cleaning at 1223K in ultra-high purity helium in order to obtain accurate reactivity/order measurements in a TGA.

Gas flow rates and CO/CO_2 ratios at the fixed bed reactor exit as a function of temperature, calculated using the model, are presented in Figure 2. As shown, the exit CO/CO_2 ratio is quite low and initially decreases with temperature until the NO becomes exhausted and the CO_2 product gas begins to gasify the carbon to CO.

The behavior of the product gases in a differential reactor will be quite different since the NO-carbon kinetic system will then operate in the very early regime noted in the fixed bed reactor profiles of Figure 1. In order to demonstrate this, we applied the same kinetic model as described above to a Montana lignite char sample reacted in a TGA. The results of the CO/CO_2 variation with temperature at a constant 0.1% burn-off are also presented in Figure 2. As shown, the CO/CO_2 ratio increases considerably with temperature due to the fact that the same level of burn-off is attained earlier in the NO conversion profile (where CO_2 is comparable to or exceeds CO) the higher the temperature. It is noted that this is precisely the same behavior found in our own TGA work [3].

Conclusions

Based on the results of the current modeling work and our own experimental experience with the NO-carbon system, we conclude the following:

(1) The CO/CO_2 product ratio can vary widely depending on the reactor system. In an integral reactor this ratio will typically be quite low and decrease slightly with temperature until the onset of CO_2 gasification of carbon. In a differential batch reactor, however, the two product gases will be of comparable magnitude, and the CO/CO_2 ratio will increase significantly with temperature at constant burn-off.

(2) The global reaction order with respect to NO, extracted from steady-state integral reaction data can be considerably less than the intrinsic

order, and may also depend on the specific reaction mechanism and rate parameter values. It can also vary with sample conditions, experimental procedures (e.g., thermal surface cleaning), and nature of the carbon surface.

Considerable care must be exercised with respect to the proper interpretation of kinetic and product composition data for the NO-carbon reaction system. Differential reactors are recommended for intrinsic kinetic studies, while integral reactors may be more useful for steady-state reactivity studies, but the kinetic data from the latter are more difficult to interpret.

References
1. L.K. Chan, A.F. Sarofim, and J.M. Beér, Comb. & Flame 52, 37 (1983).
2. J.F. Strange and P.L. Walker, Jr., Carbon 14, 345 (1976).
3. Teng, H. Ph.D. Dissertation, Brown University, 1992.
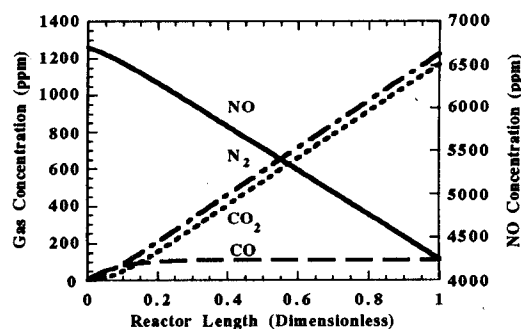
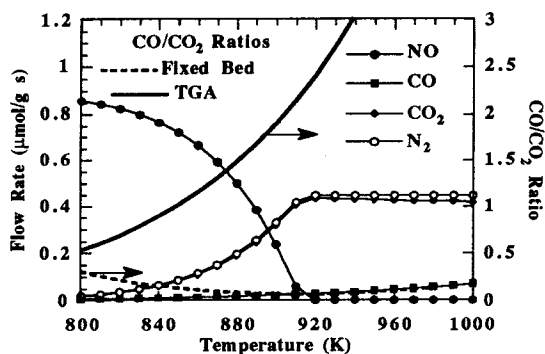Figure 1. Numerical model results for NO reduction on Montana lignite char at 873K (6700 ppm NO @ inlet).

Figure 2. Numerical model results for gas flow rates and CO/CO_2 ratios at the exit of a fixed bed reactor (Montana lignite char; feed: 10 ml/s, 6700 ppm NO). Also, CO/CO_2 ratios from simulated TGA experiments @ 0.1% burn-off.