NO REDUCTION BY CHAR: EFFECTS OF COAL RANK, BURNOUT LEVEL AND BURNOUT CONDITIONS

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Introduction

The heterogeneous reaction of NO with coal char has potential as the basis for both reburning and post-combustion clean-up processes to control NO_X emissions from coal combustion. The reaction is also very important in understanding the formation and reduction of NO during coal combustion. However, the heterogeneous kinetics and mechanism of the NO-char reaction are still poorly understood. Many questions regarding the mechanism and kinetics of the reaction, and regarding the effects of char surface area, mineral matter, coal rank, burnout, and flue gases on the reaction remain. In this work, we explore the effects of coal rank, burnout level, and burnout conditions on the kinetics of the NO-char reaction.

Experimental

The chars used in this study were prepared from 63–74 μm particles of five US standard research coals (Beulah Zap (lignite), Dietz (subB), Utah Blind Canyon (hvBb), Pittsburgh #8 (hvAb), Pocahontas #3 (lvb)) and two man-made carbons (coconut char and graphite) in a methane flat-flame burner (FFB) at a high heating rate (10^4 -10^5 K/s) and high temperature (peak temperature of 1800K). To study the effect of burnout condition on the NO-char reaction, two methods were employed to burn the chars to different burnout levels. **Method A (high temp, oxygen):** A parent char (NDL) made in the FFB is further burned out in a drop tube reactor in 3-5% O_2 and at 1800 K to different burnout levels up to 90%. Rates and kinetic data for the NO-char reaction are then measured in a packed bed reactor for these different burnout level chars. These chars were previously characterized and described by Cope (1). **Method B (low temp, NO):** Samples of the parent char are reacted in the packed bed reactor with 3050 ppm of NO and at specific temperatures (873-1173 K) to obtain samples with burnout levels up to 90%. NO-char rates and kinetics are determined directly.

The reduction of NO by char was carried out at temperatures up to 1173 K in a 10 mm ID VYCOR glass vertical packed bed reactor with a fritted quartz disc of medium porosity as a support. Each char sample was mixed with silicon carbide (inert for NO reduction), packed in the reactor, and heated in helium to the maximum temperature desired using an electric furnace. Data were collected when the quasi steady state was reached. The composition of the outlet gas was continuously monitored for N_2, CO, CO_2, N_2O, and O_2 by GC-TCD and for NO and NO_2 by a chemiluminescence NO_x analyzer (Thermo Environmental, 42H). Nitrogen and oxygen mass balances were determined between inlet and outlet streams for each run and variations always fell within ± 5%.

Results and Discussion

Effect of Coal Rank. The reaction is first order with respect to NO partial pressure and exhibits an activation energy shift from 20-40 kcal/mol at low temperatures to 45-60 kcal/mol at high temperatures for all chars studied. The low-temperature activation energy increases as coal rank increases. The shift to a distinctly different and higher activation energy at higher temperature is opposite to what would be expected if a reaction is shifting from chemical rate control to mass transfer control, and suggests different mechanisms or rate determining steps at high and low temperatures.

The low rank chars are generally more reactive than the high rank chars, as shown in Figure 1. Also, the reactivity of char seemingly depends not only on char surface area, but also on mineral content. (See also [2]).

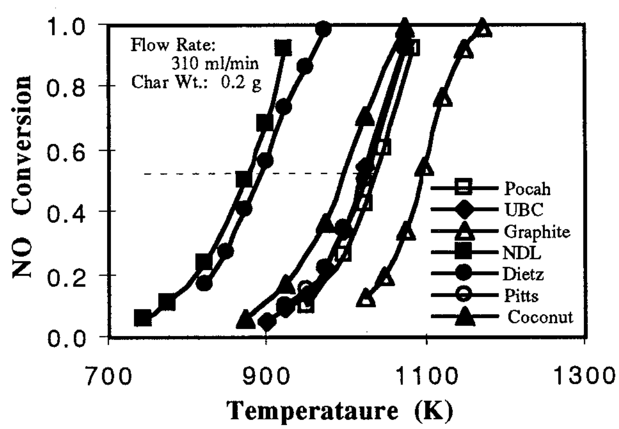

Fig. 1. Variation of NO conversion with temperature for reaction of various chars with 3050 ppm NO.

Effect of Char Burnout Conditions. As shown in Figure 2, the variation of rate constant with burnout level shows very different trends for the two different char burnout methods. For Method B, the rate constant increases as char burnout level increases. A maximum appears at 60-70% burnout level after which the rate drops off rapidly with increasing burnout. For Method A, on the other hand, the rate constant consistently and significantly decreases as char burnout level increases from 10 to 90%.

To address the different behaviors for the two different burnout conditions, both N_2 BET and CaO surface areas were determined for many of the char samples. Fairly good correlations between rate constant and both N_2 BET and CaO surface areas were found, showing that macropore structure of char (roughly measured by N_2 BET surface area) and CaO surface area (acting as a catalyst, see [2]) are probably both important factors in determining char reactivity. In Method A, high temperature and fast reaction lead to char macropores shrinking or crashing; N_2 BET surface area therefore decreases, which has also been observed by Levendis *et al* [3] in the O_2-char reaction. The decrease in CaO surface area is caused by sintering of fine CaO particles. However, low temperature favors the development of macropores and tortuous particle exterior, resulting in N_2 surface area increasing (4). CaO surface area also increases because CaO content per gram of char increases with burnout level increasing.

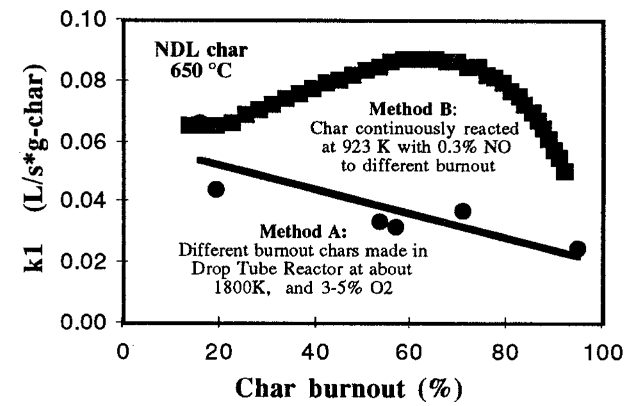

Fig. 2. Comparison of the kinetic behavior of the NO-char reaction between two burnout conditions for NDL char at 650 °C.

Effect of Burnout Level. The variations of the reaction rate with char burnout level for eight chars using the Method B burnout condition show a common feature in that the rate constant first increases with char burnout increasing, then quickly decreases. The burnout level corresponding to the maximum rate constant varies with char type. Low rank chars usually have a maximum rate at higher burnout levels than high rank chars. On a daf char mass basis, the rate constant increases almost linearly with char burnout level up to 90% burnout for all "natural" coal chars. (The two man-made carbons (graphite and coconut char) don't follow this trend.) The increasing slopes for all coal chars are roughly the same. Within burnout levels of 20-80%, the relationship between NO-char rate constant and char burnout level was found to be

$$k = k_{50} * [1 + a*(BO - 50)]$$

where k_{50} is the rate constant at 50% burnout level; a is an approximate constant (7.4×10^{-3}) for all coal chars; BO is char burnout level (%). This relationship provides a very simple way to model the rate constant for the NO-char reaction as a function of char burnout level for all "natural" coal chars.

Conclusions

For the NO-char reaction, variation of coal rank does not alter the major kinetic characterizations, e.g. reaction order and the presence of two temperature regimes with different activation energies. However, the activation energies in the low temperature regime of high rank chars were higher than those of low rank chars. Low rank chars also showed significantly higher reactivities.

Char burnout condition significantly influences the kinetics of the NO-char reaction. Burnouts achieved at high temperatures and in oxygen lead to decreases in BET and CaO surface areas and corresponding decreases in reaction rate constant for the NO-char reaction. On the other hand, burnouts achieved at low temperatures in NO are apparently beneficial to the development of char macropores and CaO surface area so that both types of surface area increase as char burnout level increases. These correspondingly result in increases in the NO-char reaction rate up to char burnout levels of about 90%.

For burnouts achieved at low temperature by reacting with NO (Method B), the rate constant (per char mass) for the NO-char reaction increases almost linearly with char burnout level up to 90% burnout for all natural coal chars studied. The ratio of increase between 20 and 80% burnout levels is roughly the same for all chars studied, which provides a simple way with moderate accuracy to model the variation of the rate with char burnout level.

Acknowledgments

This work was sponsored by the Advanced Combustion Engineering Research Center at Brigham Young University. Funds for this center are received from the National Science Foundation, the State of Utah, the U.S. Department of Energy, and a number of industrial participants. We also thank Richard F. Cope for char preparation and Troy Ness for technical assistance.

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