POPULATION AND TURNOVER NUMBER OF ACTIVE POTASSIUM SITES ON BITUMINOUS COALS DURING GASIFICATION

C. T. Ratcliffe*

Corporate Research-Science Laboratory
Exxon Research and Engineering Company
Route 22 East, Annandale, N.J. 08801

S. N. Vaughn

Exxon Research and Engineering Company
P. O. Box 4255
Baytown, Texas 77520

Introduction

The activity of alkali metal salts as catalysts for steam gasification on carbon surfaces has been well documented.[1-2] The kinetics of catalyzed gasification with potassium salts on carbon and the data obtained from characterizing alkali metal treated carbon is consistent with potassium in a highly dispersed and ionic state.[3-5]

The rate of potassium catalyzed gasification on bituminous coals, when plotted as a function of carbon conversion, tends to decrease at higher carbon conversions and can be highly variable depending on the source of coal and method of catalyst treatment. The mechanism(s) of catalyst deactivation are not well understood; loss of potassium sites due to reaction with mineral matter, limited mobility after initial reaction, detachment from the coal surface and collapse of pore structure have all been suggested as reasons.[6-8] A key factor in developing a fundamental understanding of the change in rate behavior will be the ability to accurately count the population of active alkali sites during gasification as a function of carbon conversion.

We have recently found that carbon dioxide chemisorbs in an irreversible manner on the surface of potassium treated Spherocarb, a high surface area carbon.[9] The molar quantity of CO_2 adsorbed on this surface at 300°C, after initial thermal treatment at 850°C, correlated with the level of potassium loading and suggested a facile method of measuring alkali dispersion. The value of 0.5 to 0.6 adsorption sites per K_2O impregnated on the surface also agreed with the initial number of active sites measured by the derivitization technique.[10]

The purpose of this investigation has been to establish CO_2 chemisorption as a tool to selectively measure the population of active alkali sites on gasified coal chars and to determine the specific activity or turnover number of the active sites under gasification conditions.

* Current address: Union Oil Company of California, Union Science and Technology Division, P. O. Box 76, Brea, California, 92621.

Experimental

Samples of bituminous coals were obtained in 5 gallon containers from the mines under a nitrogen atmosphere. The coals are identified by mine and state as: Monterey No. 1, Illinois #6, Hawk's Nest, Colorado; Valley Camp, Utah; Walden, Colorado. The samples were sealed in an inert atmosphere for shipment and opened in a controlled atmosphere dry box. Impregnation of the coals with aqueous solutions of potassium carbonate or potassium hydroxide were performed in a controlled atmosphere environment by the method of incipient wetness. Alkali salts were obtained commercially (reagent grade K_2CO_3, ultra pure KOH,) with aqueous solutions prepared immediately before impregnation. After impregnation, the samples were dried under inert atmosphere and stored in sealed glass vessels. While an apparent dispersion was observed with all KOH treated coals, the K_2CO_3 treated coals required rewetting the samples, followed by stirring and drying to obtain an even dispersion of K_2CO_3. The loading of potassium was in the range of 7-10%.

Adsorption and gasification studies were performed with a Mettler 2000C TGA/DSC thermal analysis unit equipped with a corrosive gas head [9] and a DuPont 951 TGA unit with a pressurized housing for operation up to 500 psig (Figure #1).

Technique for Adsorption, Gasification

The adsorption properties of bituminous coal and catalyzed coal samples were measured by means of the following procedure. A sample of approximately 80 milligrams was loaded into a ceramic crucible with an equivalent amount of SP-1 graphite prepared in a crucible of identical color and approximately the same mass. The preweighed crucibles were loaded onto the TGA/DSC platform and outgassed at ambient temperature by mild evacuation (10^{-3}mm) for one half hour. The sample and reference material were subsequently temperature programmed at 29.9°/min. to 850°C in flowing helium. After heat treatment, samples were cooled to the desired temperature of 300°C for adsorption studies. While the sample was maintained at the selected isothermal temperature, a measured flow of CO_2 was introduced into the helium carrier. The reactive gas flow, as measured by the Tylan flow meter, was maintained at 2cc per minute with the carrier flow of 20cc per minute helium; thus a partial pressure ratio of 1:10 of CO_2 to inert carrier was utilized during the adsorption study.

Adsorption of CO_2 was monitored by weight gain recorded on a strip chart. Adsorption was normally rapid with a plateau in total weight reestablished in 15-30 minutes. The mixed gas stream was replaced with a pure helium stream with a second period of 10-15 minutes allowed for any subsequent change in weight. The total adsorbed gas could thus be divided into physical and chemical adsorbed fractions as the former was desorbed when the reactive gas was replaced by helium and the latter was retained as a net weight gain.

A measured flow of CO_2 or H_2O vapor was mixed with the He carrier gas flows and the temperature of the sample was raised to an isothermal value of 700-800°C to perform partial gasification of the char. After a steady state period was established, the rate of weight loss per unit time was obtained. The reactive gas flow was subsequently terminated and the above described procedure was repeated for CO_2 measurement of the active site density.

High pressure measurements were performed on a modified DuPont 951 TGA which had been enclosed in a pressurized housing (Figure 1). A similar procedure was used to obtain the rate of gasification; the reactive gas composition was 30% H_2O, 7% CO, 13% CO_2, 15% CH_4 and 35% H_2. Operating conditions were 500 psig and 705°C. Adsorption measurements with CO_2 were obtained at 300°C, one atmosphere pressure, by the procedure described above with a flow of N_2 as the inert carrier gas.

Results and Discussion:

Adsorption of CO_2 was examined on each of the neat coals after thermal treatment to 850°C. While physisorption was observed at lower temperatures (100°C) in all cases, only Walden and Valley Camp chars revealed any measureable chemisorption at 300°C. The thermal desorption profile of Walden or Valley Camp chars after CO_2 adsorption identified $CaCO_3$ formation from CO_2 interaction with CaO as the source of the chemisorption. The quantity of CO_2 was always an order of magnitude lower than adsorption on alkali treated chars. A display of the quantity of CO_2 adsorbed on K_2CO_3 and KOH treated coals is shown in Figures 2 and 3. The molar quantity of CO_2 adsorbed (measured by TGA) has been normalized with the molar quantity of impregnated potassium salt to represent relative dispersion values on the ordinate axes. As the chemisorption measurement with CO_2 is performed after each thermal heat cycle to 850°C in inert atmosphere, only active potassium sites which are bonded to the carbon will chemisorb CO_2. Any free potasium oxide, hydroxide, or basic salt will irreversibly adsorb CO_2 on the first cycle and remain as thermally stable K_2CO_3. Thus, the efficacy of the technique is its ability to selectively measure only the active potassium complexes bonded to the carbon surface, as they regenerate on each thermal heating cycle to 850°C in He.

The similarity of the four bituminous coals in their number of available active sites is in contrast to the higher and more constant value of K_2CO_3 impregnated Spherocarb ($800m^2/g$, mineral free amorphous carbon) as shown in the dotted line of Figure #2. The low population of active sites on the KOH and K_2CO_3 treated coal chars may represent a limited surface area, as recently reported by Shadman.[11] The lower initial values on KOH - coals do not correspond to lower surface areas with our BET measurements, but do correlate in a positive manner with lower volatile matter release on initial thermal tereatment. Deposition of carbon or non-volatile carbonaceous residue on the active base sites may limit the availability of alkali after initial thermal treatment. Franklin, Peters and Howard have detailed the effect of mineral matter and especially in exchanged alkali on reducing the volatile matter and tar upon pyrolysis of bituminous and sub-bituminous coals.[12-14] The greater reduction in volatile matter with KOH vs. K_2CO_3 treated coals, due to the stronger base, most probably results in a higher localized coating of condensed tar on the active alkali sites. The temporary "poisoning" of the sites to CO_2 adsorption in KOH or K_2CO_3 treated chars is removed after the initial 5-10% gasification.

The maximum population of sites in the 20-50% char conversion range, representing about 30% dispersion of K_2O, is only one-half the value obtained with potassium impregnated Spherocarb. Interaction of the basic potassium salts with the mineral matter may well have consumed a portion of the impregnated salt (7) in addition to a possible lower dispersion of the salts on the lower surface area chars. The decline in the site population at 60-90% carbon conversion indicates the continued neutralization of the alkali with mineral matter in addition to the detachment of alkali from the carbon.

When the rate of gasification with CO_2 is corrected for the population of active sites at each level of char conversion, a specific activity or turnover number can be obtained. The turnover number for Valley Camp and Hawk's Nest coal (both impregnated with KOH) as a function of char conversion are shown in Figure #4 for CO_2 gasification. The constant value of the turnover number for the entire range of char conversion now establishes the density of active potassium sites as the rate controlling parameter in CO_2 gasification of these coals. While the results in Figure #4 clearly remove the quantity of carbon in the char as a rate controlling parameter, the change in the concentration or composition of the vapor phase reactant atmosphere is also known to affect catalyzed gasification. Samples of the same impregnated Valley Camp and Hawk's Nest coals have been studied under high pressure conditions with a reactive atmosphere typical of a fluid bed steam/coal gasification environment. The plot of turnover number vs char conversion under this set of reaction conditions is shown in Figure #5. The difference in the average turnover number shown for the two sets of gasification conditions can be attributed to differences in reactivity of the two gas atmospheres. It is again obvious that the constant turnover number for potassium over the range of char conversion confirms the rate controlling nature of the potassium site density for coal gasification.

Summary:

Chemisorption of CO_2 at 300°C provides a selective and rapid technique to measure the active site density of alkali catalysts on coal at intermittent periods of coal gasification. With a thermal balance/reactor, the specific activity per catalyst site (turnover number) has been measured for catalyzed gasification of CO_2 or steam/product gases with bituminous coals. The site density of potassium on carbon as the rate controlling parameter in gasification of coal as shown by a constant value for the turnover number over the full range of char conversion.

REFERENCES

1. International Symposium, Fundamentals of Catalytic Coal and Carbon Gasification, Special Issue, Fuel, 62, 1-261 (1983)
2. For Review, D. W. McKee, Chem. Phys. of Carbon, 16, 1-118 (1981)
3. C. A. Mims, J. J. Chludzinski, J. A. Pabst, R. T. K. Baker, J. Catalysis, 88, 97 (1984)
4. F. J. Long, K. W. Sykes, J. Chim. Phy., 47, 361 (1950)
5. C. L. Spiro, D. W. McKee, P. G. Kosky, E. J. Lamby, Fuel 63, 686, (1984)
6. F. Kapteijn, J. A. Moulijn, Fuel 62, 205, (1963)
7. L. Kuhn, H. Plogmann, Fuel, 62, 205 (1983)
8. D. Douchanov, G. Angelova, Fuel 62, 231 (1983)
9. C. T. Ratclffe, Proceedings of the 13th North American Thermal Analysis Society, p.90, September 23-26, 1984, Philadelphia, PA
10. C. A. Mims, K. D. Rose, M. T. Melchior, J. A. Pabst, J. Am. Chem. Soc., 104, 886 (1982)
11. F. Shadman, D. A. Sams, Div. of Fuel Preprints, 29(2), 160 (1984)
12. H. D. Franklin, W. A. Peters, J. B. Howard, Fuel, 61, 155, (1982)
13. Ibid, 1214
14. H. D. Franklin, R. G. Cosway, W. A. Peters, I&EC Process Des. Dev., 22, 42 (1983)

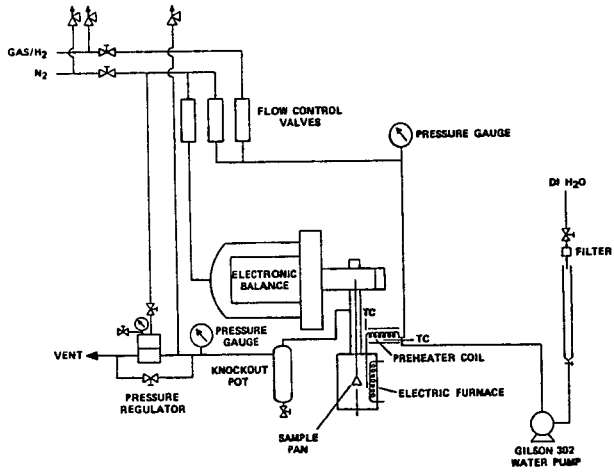

Figure 1. High Pressure TGA Reactor System for Char Gasification

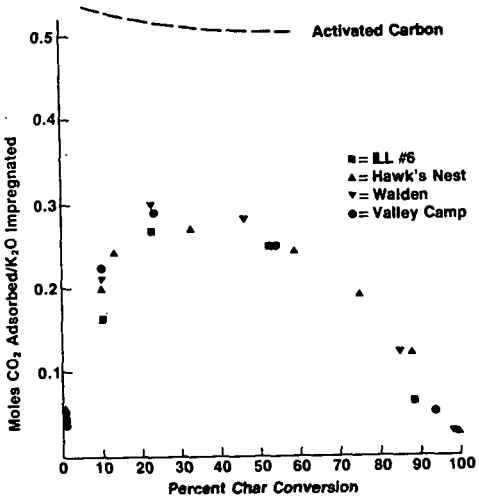

Figure 2, Dispersion of KOH treated coal chars vs carbon conversion as measured by CO_2 chemisorption at 300°C.

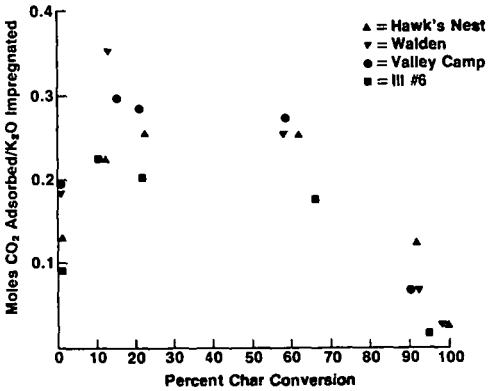

Figure 3. Dispersion of K_2CO_3 Treated coal chars vs carbon conversion as measured by CO_2 chemisorption at 300°C.

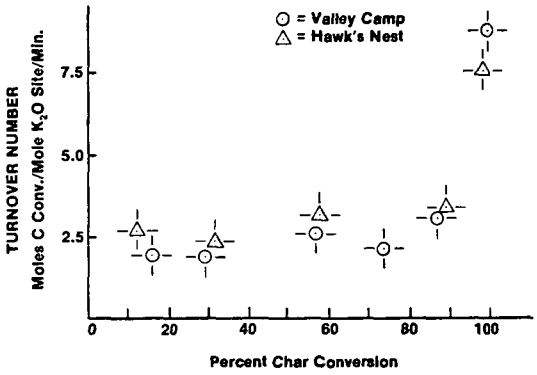

Figure 4. Specific activity per site of KOH treated coals v carbon conversion; CO_2 gasification, ⊙ Valley Camp, △ Hawk's Nest.

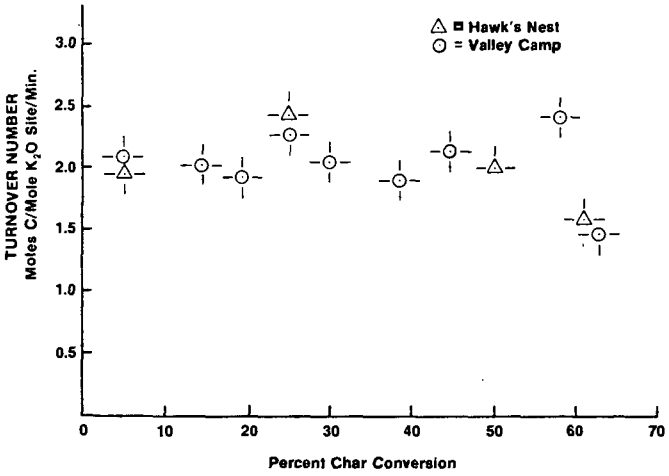

Figure 5. Specific activity per site of KOH treated coals vs carbon conversion; H_2O/CO_2/recycle atmosphere gasification, 500 psig, vs carbon conversion; ⊙ Valley Camp, △ Hawk's Nest.