

# A CURRENT VIEW OF THE MECHANISM FOR THE CATALYTIC GASIFICATION OF COAL CHAR

Bernard J. Wood and Kenneth M. Sancier

Materials Research Laboratory, SRI International  
333 Ravenswood Avenue, Menlo Park, CA 94025

## INTRODUCTION

The addition of modest quantities of certain inorganic salts to coal substantially promotes its reactivity with steam or carbon dioxide. Because of the cost of the added salt and the addition of process steps for admixture and recovery, technoeconomic analysis predicts that this catalytic coal gasification process can be of practical value only in cases where the maximum process temperatures are limited by outside constraints.[1] One such case is the production of methane, where high equilibrium yield is favored by lower temperatures.[2] Current predictions, based on natural gas demand and reserves, suggest that methane from coal will not be needed in the next 25-50 years. Consequently, industrial interest in the catalytic gasification of coal, once high, has waned, and full-scale development of the process has been given lower priority.

Another potentially attractive application of the catalytic gasification process is the utilization conversion, storage, and transport of heat produced by a gas-cooled nuclear reactor where the attainable coolant temperature has an upper limit of about 950°C.[3] Implementation of this technology is being considered[4], but large-scale application lies some distance in the future.

However, the low probability of near term applications has not hampered scientific interest in the process. In the last few years, many investigators have studied the process, using a wide variety of approaches and tools. Since 1980 more than 100 papers have been published on the subject of the mechanism of catalytic gasification of char or carbon.[5] This investigative activity has given us sufficient insight into the process to suggest a detailed mechanism that defines the nature and role of the catalyst during gasification.

## CHARACTERISTICS OF CATALYST ACTION

Effective coal/char gasification catalysts are ionic salts with oxygen-bearing anions (or anions that are converted to oxygen-containing species under gasification conditions). The cations of the salt react

with the carbonaceous material to form a chemically and thermochemically distinct active species that mediates the gasification process. The anions of the salt may modify the pathway of formation of the active species, but for all effective salts this species is certainly formed at sub gasification temperatures.

There is broad agreement among recent investigators that the catalyst supplies oxygen to the carbon. Many investigators favor involvement of a redox cycle in which the catalyst is reduced by the carbon and oxidized by the gaseous reactant, but few speculate on a detailed mechanism. Nevertheless, there are a number of details of the gasification reaction system for which evidence is particularly strong:

- The working catalyst forms a liquid film that wets the carbon surface;
- The molten catalyst is a metal-rich (oxygen deficient) compound, probably an oxide, over which the metal vapor pressure has a characteristic equilibrium value;
- Chemical attack by the catalyst and during gasification occurs at the carbon atoms on edges of aromatic arrays;
- The reduction step occurs by donation by the carbon of an electron to the catalyst phase, neutralizing the cationic charge;
- A metal-oxygen-carbon complex analogous to a phenolate salt is a reaction intermediate;
- The intermediate is a precursor of gaseous CO production by a decarbonylation step that is likely rate governing.

#### A PROPOSED MECHANISM

Based on these considerations, we have devised a detailed mechanism of catalyst action. Dispersion of the catalyst is a critical initial step that occurs at subgasification temperatures when the catalyst becomes a liquid film that wets the carbon and spreads over its exposed surface. Evidence for such a process comes from microscopic studies[6-8], measurements of surface area changes,[9,10] and the observed increase in electrical conductance upon heating of carbon-catalyst admixtures,[10] indicative of the formation of a phase with high charge carrier mobility. More quantitative information about the nature of alkali metal carbonates admixed with carbon is obtained from Knudsen cell mass spectrometry.[11] At about 900 K, both carbon-K<sub>2</sub>CO<sub>3</sub> and carbon-Cs<sub>2</sub>CO<sub>3</sub> admixtures in a Knudsen cell gradually lose oxygen, as evidenced by a progressive diminution in the equilibrium partial pressures of CO and CO<sub>2</sub>. At the same time the pressure of the alkali metal increases, indicating an increase in thermodynamic activity possibly produced by a change in metal/oxygen stoichiometry. Opposite changes occur when steam

or  $\text{CO}_2$  is admitted to the Knudsen cell. These observations suggest that the liquid film in contact with the carbon is a non-stoichiometric oxide that contains an excess of the metal as atoms in a dissolved state. During gasification, the composition of the film is determined by a dynamic balance between a reducing process at the carbon-catalyst interface and an oxidizing process at the surface in contact with the gaseous reactant. The composition and characteristics of some Cs-rich oxides have been characterized as crystalline solids at room temperature.[12] At high temperatures they melt into liquid phases (for which free energies of formation have been evaluated) comprised of a higher oxide containing excess Cs.[13] Using the equilibrium partial pressures of Cs and CO measured over a  $\text{Cs}_2\text{CO}_3$ -carbon sample in the Knudsen cell, together with the published thermochemical data[13], we estimated the composition of the liquid phase to be  $\text{Cs}_4\text{O}$ . [11] A similar analysis of the  $\text{K}_2\text{CO}_3$ -carbon system was not possible because of the lack of thermochemical data at low oxygen partial pressures. By analogy, however, all alkali-metal-oxygen systems would be expected to behave in a parallel fashion. Further, very recent evidence of the conversion of  $\text{K}_2\text{CO}_3$  to a nonstoichiometric oxide in the presence of carbon is provided by studies with isotope-labelled catalysts.[14]

The existence of an oxide with an excess of the alkali-metal component requires an equivalent number of oxygen vacancies. Thus, the affinity of this phase for reaction with an oxidizing gas will be proportional to the alkali metal activity. Oxygen ions produced by this reaction between the catalyst phase and an oxidizing gas are transported to the carbon/catalyst interface by diffusion, a process that is fast at gasification temperatures. One principal product of steam gasification,  $\text{H}_2$ , would be formed at the catalyst/steam interface.

The reaction steps occurring at the carbon/catalyst interface require some explanation because the carbon structure is comprised to some degree of planar aromatic arrays, and aromatic hydrocarbons are known to be quite unreactive toward oxide and hydroxide ions. Transmission electron microscopy[7,8] has confirmed that the catalyst interacts with carbon atoms located at the edges of the planar arrays, but the mechanism of the attachment remains obscure. We suggest that the initial reaction step is a simple electron transfer from the aromatic material to the alkali metal ion of the catalyst. Recently reported[15] measurements made in an electrochemical cell with a molten  $\text{Na}_2\text{CO}_3$  electrolyte provide strong evidence for such an electron transfer step. In this work, the addition of graphite to the electrolyte (in the absence of air) rapidly shifted the rest potential of the cell from -0.511 to -1.348 V, indicative of the formation of an easily oxidized species, such as sodium metal, due to reduction of the sodium ions in the carbonate by the solid carbon. This process produces directly an excess of metal atoms in the catalyst and leaves the carbon array with a net positive charge, termed a radical cation. Such a species would be highly reactive toward the negatively charged oxygen ions in the catalyst. It is highly probably that reaction of the radical cation and the  $\text{O}^-$  leads to formation of a phenolate ion, the presence of which in

the carbon array has been confirmed.[16] Indeed, phenolate ion structures would be stabilized by alkali metal ions in the molten catalyst film. The existence of some type of K-O-C structure has been suggested also on the basis of infrared spectra of partially gasified  $K_2CO_3$ -char admixtures.[17,18]

The rate of formation of CO during char gasification has been correlated with the concentration of phenolate groups.[19] This observation, in conjunction with the observed stability and steady state population of these groups at gasification temperatures,[20] suggests that decomposition of the phenolate groups is the rate-governing step in the catalytic gasification process. Decomposition may occur through conversion of the phenol functionality to the ketone followed by thermolytic decarbonylation.[10] This part of the gasification reaction pathway remains speculative, although such decarbonylation reactions have been observed to occur at high temperatures.[21]

### CONCLUSION

Inorganic salts composed of alkali metal cations and oxygen-bearing anions are effective catalysts for the steam or  $CO_2$  gasification of coal char. Under gasification conditions the catalyst is converted to a nonstoichiometric oxide that is highly dispersed over the char surface as a liquid film. This catalyst film mediates the transfer of oxygen from the oxidizing gas to the char surface by way of a redox cycle. At the catalyst/char interface, electron donation by the char reduces the cation to a neutral metal atom dissolved in the catalyst, leaving a positively-charged radical cation on the char surface. The radical cation reacts readily with oxygen ions from the catalyst forming a phenolate functionality that is stabilized by the metal ions in the catalyst phase. The oxygen ions lost from the catalyst are replenished at the gas/catalyst interface by oxidation of the dissolved metal atoms by the oxidizing gas. The reactive intermediates are transported between gaseous oxidant and char by diffusion through the catalyst phase. CO is formed by decarbonylation of the phenolate species, a process that governs the rate of the gasification reaction.

### ACKNOWLEDGEMENT

Our studies of the mechanism of catalytic gasification of char were supported by the U.S. Department of Energy, Morgantown Energy Technology Center under Contract No. DE-AC21-80MC14593.

### REFERENCES

- [1] H. Juntgen, Fuel, 62 (2), 234 (1983).
- [2] N. C. Nahas, Fuel, 62 (2), 239 (1983).
- [3] H. Kubiak, H. J. Schroter, A. Sulimma, and K. H. van Heek, Fuel, 62 (2), 242(1983).

- [4] D. A. O'Sullivan, Chem. & Eng. News 62(10), 20-21 (1984).
- [5] B. J. Wood and K. M. Sancier, Catal. Rev. Sci. Eng., in press (1984).
- [6] H. Marsh and I. Mochida, Fuel, 60 (3), 231 (1981).
- [7] D. J. Coates, J. W. Evans, A. L. Cabrera, G. A., Somorjai, and H. Heinemann, J. Catalysis, 80, 215 (1983).
- [8] C. A. Mims, R. T. K. Baker, J. J. Chludzinski, and J. K. Pabst, Preprints Am. Chem. Soc. Fuel Chem. Div., 28 (1), 71 (1983).
- [9] K. Otto, L. Bartosiewicz, and M. Shelef, Fuel, 58 (8), 565 (1979).
- [10] B. J. Wood, R. H. Fleming, and H. Wise, Fuel, in press (1984).
- [11] B. J. Wood, R. D. Brittain and K. H. Lau, Carbon, in press, (1984).
- [12] A. Simon, Structure and Bonding (Berlin), 36, 81 (1979).
- [13] C. F. Knights and B. A. Phillips, J. Nuclear Mat., 84, 196 (1979).
- [14] J. M. Saber, J. L. Falconer, and L. F. Brown, private communication
- [15] G. B. Dunks, Proceedings International Conference on Coal Science, Pittsburgh (1983), p. 457.
- [16] C. A. Mims, K. D. Rose, M. T. Melchior, and J. K. Pabst, J. Am. Chem. Soc. 104, 6886 (1982).
- [17] I. L. C. Freriks, H. M. H. van Wechem, J. C. M. Stuiver, and R. Bouwman, Fuel 60, 463 (1981).
- [18] S. J. Yuh and E. E. Wolf, Fuel 62, 252 (1983).
- [19] C. A. Mims and J. K. Pabst, Am. Chem. Soc. Fuel Chem. Div. Preprints 25(3), 258 (1980).
- [20] C. A. Mims and J. K. Pabst, Fuel, 62 (2), 176 (1983).
- [21] G. Schaden, Proc. 3rd. International Symp. Analyt. Pyrolysis, C.E.R. Jones and C. A. Cramers, editors, Elsevier, New York, 1977, p. 289.