

# The Mechanism of the Catalytic Gasification of Carbons: The Current State of Our Understanding

Bernard J. Wood  
SRI International  
Menlo Park, CA 94025

## Introduction

Catalytic gasification is a term that is rather loosely applied to a variety of processes using inorganic additives to promote the kinetics of conversion of carbon to gaseous products. In recent years, interest in the catalytic gasification of coal by steam to produce syngas or methane has generated many studies of the mechanism of this process. This body of work covers a great variety of catalyst-carbon systems studied with a broad array of experimental tools. The results represent a formidable body of evidence that provides strong support for a number of essential catalyst characteristics and for specific elementary process steps. Taken together, these considerations form the basis for a detailed mechanism of catalyst action.

## Characteristics and Operation of an Effective Catalyst

An effective catalyst is an ionic salt containing an oxygen-bearing anion. Many investigations have shown that the carbonate, hydroxide, oxide, acetate, sulfate, and nitrate salts of the alkali and alkaline earth metals are generally effective catalysts, in strong contrast to the halides which exhibit little catalytic activity.<sup>1-5</sup> However, the halides become active catalysts under conditions where they are hydrolyzed or otherwise converted to a species containing an oxygen-bearing anion.<sup>3,6-8</sup>

The working catalyst must form a liquid film that wets the carbon surface. 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,<sup>9-12</sup> measurement of surface area changes,<sup>13,14</sup> and an observed increase in electrical conductance upon heating of carbon-catalyst admixtures,<sup>14</sup> indicative of the formation of a phase with high charge carrier mobility.

The molten catalyst is a metal-rich (oxygen-deficient) compound. The nature of the high temperature chemical state of alkali metal carbonates admixed with carbon can be inferred from Knudsen cell mass spectrometric measurements.<sup>7</sup> 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 progress diminution in the equilibrium partial pressures of CO and CO<sub>2</sub>. At the same time the pressure of the alkali metal in-

creases, indicating an increase in thermodynamic activity possibly produced by a change in metal/oxygen stoichiometry. Opposite changes occur when steam or CO<sub>2</sub> 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.<sup>15</sup> 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.<sup>16</sup> Using the equilibrium partial pressures of Cs and CO measured over a Cs<sub>2</sub>CO<sub>3</sub>-carbon sample in the Knudsen cell, together with the published thermochemical data, we estimated the composition of the liquid phase to be Cs<sub>4</sub>O.<sup>7</sup> A similar analysis of the K<sub>2</sub>CO<sub>3</sub>-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 K<sub>2</sub>CO<sub>3</sub> to a non-stoichiometric oxide in the presence of carbon is provided by studies with isotope-labelled catalysts.<sup>17</sup>

Chemical attack by the catalyst and during gasification occurs at the carbon atoms on the edges of aromatic arrays. 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 these surfaces are known to be quite unreactive toward oxide and hydroxide ions.<sup>18</sup> Transmission electron microscopy 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.<sup>10-11</sup>

The catalyst is reduced at the carbon-catalyst interface. 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 measurements made in an electrochemical cell with a molten Na<sub>2</sub>CO<sub>3</sub> electrolyte provide strong evidence for such an electron transfer step.<sup>19</sup> 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.

A metal-oxygen-carbon complex is formed by the reaction of the charged species at the interface. The positively charged radical cation would be highly reactive toward the negatively charged oxygen ions in the catalyst. It is highly probable that reaction of the radical cation and the  $O^{2-}$  leads to formation of a phenolate ion, the presence of which in the carbon array has been confirmed.<sup>20</sup> 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.<sup>5,21</sup>

The metal-oxygen-carbon complex is a precursor of gaseous CO production. The rate of formation of CO during char gasification has been correlated with the concentration of phenolate groups.<sup>22</sup> This observation, in conjunction with the observed stability and steady state population of these groups at gasification temperatures suggests that decomposition of the phenolate groups is the rate-governing step in the catalytic gasification process.<sup>23</sup> Decomposition may occur through conversion of the phenol functionality to the ketone followed by thermolytic decarbonylation.<sup>14</sup> This part of the gasification reaction pathway remains speculative, although such decarbonylation reactions have been observed to occur at high temperatures.<sup>24</sup>

#### Conclusion

Inorganic salts composed of alkali metal cations and oxygen-bearing anions are effective catalysts for the steam or  $CO_2$  gasification of carbon. Under gasification conditions the catalyst is converted to a non-stoichiometric oxide that is highly dispersed over the carbon surface as a liquid film. This catalyst film mediates the transfer of oxygen from the oxidizing gas to the carbon surface by way of a redox cycle. At the catalyst/carbon interface, electron donation by the carbon reduces the cation to a neutral atom dissolved in the catalyst, leaving a positively-charged radical cation on the carbon 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 carbon 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.

#### References

1. M. J. Veras and A. T. Bell, *Fuel* **57**, 194 (1974).
2. D. W. McKee, *Fuel* **62**(2), 170 (1983).
3. P. G. Kosky, E. J. Lamby, D. H. Maylotte, D. W. McKee, and C. L. Spiro, "Coal Gasification Mechanisms. Final Report," DOE/MC/14591-1397, U. S. Dept. of Energy, Morgantown, WV (November, 1982).
4. L. R. McCoy, R. C. Ampaya, R. C. Sanders, D. Stelman, L. A. Heredy, C. A. Trilling, I. B. Goldberg, K. E. Chung, E. H. Cirlin, D. S. Carroll, J. J. Ratto, C. M. Jantzen, and T. M. McKinney, "Investigation of Coal Gasification Catalysis Reaction Mechanism. Final Report," DOE/MC/14592-1419, U. S. Dept. of Energy, Morgantown, WV (August, 1982).
5. S. J. Yuh and E. E. Wolf, *Fuel* **62**, 252 (1983).
6. C. A. Mims and J. K. Pabst, *Am. Chem. Soc. Fuel Chem. Div. Prepr.* **25**(3), 258 (1980).
7. B. J. Wood, R. D. Brittain and K. H. Lau, *Carbon*, In Press.
8. S. J. Yuh and E. E. Wolf, *Fuel*, In Press.
9. H. Marsh and I. Mochida, *Fuel* **60**(3), 231 (1981).
10. D. J. Coates, J. W. Evans, A. L. Cabrera, G. A. Somorjai, and H. Heinemann, *J. Catalysis* **80**, 215 (1983).
11. C. A. Mims, J. J. Chludzinski, J. K. Pabst, and R.T.K. Baker, *J. Catalysis* **88**, 97 (1984).
12. C. L. Spiro, D. W. McKee, P. G. Kosky, and E. J. Lamby, *Fuel* **63**, 686 (1984).
13. K. Otto, L. Bartosiewicz, and M. Shelef, *Fuel* **58**(8), 565 (1979).
14. B. J. Wood, R. H. Fleming, and H. Wise, *Fuel* **63**(11), 1600 (1984).
15. A. Simon, *Structure and Bonding* (Berlin) **36**, 81 (1979).
16. C. F. Knights and B. A. Phillips, *J. Nuclear Mat.* **84**, 196 (1979).
17. J. M. Saber, J. L. Falconer, and L. F. Brown, *J. Catalysis* **90**, 65 (1984).
18. C. Wong and R. T. Yang, *Ind. Eng. Chem. Fundam.* **23**, 298 (1984).
19. G. B. Dunks, *Proceedings International Conference on Coal Science*, Pittsburgh (1983), p. 457.
20. C. A. Mims, K. D. Rose, M. T. Melchior, and J. K. Pabst, *J. Am. Chem. Soc.* **104**, 6886 (1982).
21. I.L.C. Freriks, H.M.H. van Wechem, J.C.M. Stuiver, and R. Bouwman, *Fuel* **60**, 463 (1981).
22. C. A. Mims and J. K. Pabst, *Am. Chem. Soc. Fuel Chem. Div. Preprints* **25**(3), 258 (1980).
23. C. A. Mims and J. K. Pabst, *Fuel* **62**(2), 176 (1983).
24. G. Schaden, *Proc. 3rd. International Symp. Analyt. Pyrolysis*, C.E.R. Jones and C. A. Cramers, Editors, Elsevier, New York, p. 289 (1977).