Effect of Small Concentrations of CO on Rate of Gasification of Spectroscopic Graphite in O₂

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Introduction

In CO₂ gasification of carbon, reactions (1) to (3), CO inhibits via reaction (2).¹

\[ \text{CO}_2 + \text{C} + \text{C}(\text{O}) + \text{CO} \]  
\[ \text{C}(\text{O}) + \text{CO} \to \text{CO}_2 + \text{C} \]  
\[ \text{C}(\text{O}) + \text{CO} \to \text{CO} + \text{C} \]  

Reactions (2) and (3) are common to O₂ gasification of carbon. Although reaction (2) alters the CO₂/CO product ratio during steady state O₂ gasification of carbon², CO inhibition of O₂ gasification of carbon has not been reported. During a recent study, the possibility of CO inhibition was raised.³ The conditions under which CO inhibition may be found for O₂ gasification of carbon were explored.

Experimental

The same flow reactor was used for the entire experiment. Gasification rates were calculated from the total gas flow and the changes in the CO and CO₂ concentrations (measured by non-dispersed infrared absorption). Rates are normalized to the amount of carbon remaining. SP-1, a purified natural graphite powder produced by Union Carbide having an impurity level <1 ppm was supported on high purity quartz or alumina trays. Gases include Ar (>99.999%) which was passed through a Zr alloy gettering furnace, hydrocarbon-free O₂ (>99.99%) with a H₂O <3 ppm, and a CO/CO₂/air mixture which had the CO₂ and H₂O removed by absorption. As received samples were heated in flowing Ar at 1234K for 4h, then gasified to ~20% burn-off in 0.1 MPa O₂ at 840 ±3K. Some of these samples were tested directly. Others were heated in Ar as before and given a small burn-off in 0.1 MPa O₂ at 840 ±3K. CO additions and Ar additions were performed with total pressure = 0.1 MPa, temperature = 840 ±3K, and total flow = 0.6 l/min (STP). Additional burn-off during testing was <4%.

Results and Discussion

In Table 1 and Figure 1, the first burn-off value is the total, the second is the burn-off since the most recent heat treatment. Also listed are the CO₂/CO ratio with no added CO and the average weight. Runs in Ar/O₂, with no added CO, showed that the product outlet concentrations were essentially unchanged as the inlet O₂ concentrations were varied over the small ranges given in Table 1. Blank runs with no graphite in the tray showed that ~5% of the inlet CO was oxidized regardless of its inlet concentration. At constant outlet CO, lower weight samples and those not recently heat treated, runs 142 and 156, have higher reactivities and higher CO₂/CO ratios. This indicates catalytic influence, intrinsic⁴ and/or extrinsic⁵.

Uncatalyzed gasification be will be inhibited by CO to the extent that reaction (2) competes with reaction (3). The effect of CO on catalyzed gasification is not clear. Catalyzed CO oxidation occurs for the more reactive samples. It is likely that gasification catalysis results from an increased supply rate of atomic O. CO can retard the supply rate by competing with O₂ for catalyst active sites and by reacting with the O. CO can accelerate the O supply rate by heating the impurity particle via catalyzed CO oxidation. This acceleration would be more significant for greater levels of impurity and greater levels of added CO. All of these complications are depicted in Figure 1.

CO inhibition of the steady state C-O₂ reaction is found when the gasification is dominated by the uncatalyzed reaction. When the catalyzed reaction becomes significant, the effect of CO is complicated by heat generated from its catalytic oxidation.

Acknowledgements

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Figure 1. Effect of CO on Reactivity of Various Graphite Samples.

Table 1. Effects of CO Addition During Graphite Gasification in O₂

<table>
<thead>
<tr>
<th>Oxygen Conc. (%)</th>
<th>Inlet Concentration (ppm)</th>
<th>Outlet Concentration (ppm)</th>
<th>Net. Concentration (ppm)</th>
<th>CO Oxidized (%)</th>
</tr>
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<tr>
<td></td>
<td>CO₂</td>
<td>CO</td>
<td>CO₂</td>
<td>CO</td>
</tr>
<tr>
<td>Run 132B: 29.2% (4.7%) burn-off, 10.02 g sample, CO₂/CO = 1.2</td>
<td></td>
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<tr>
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<td>830</td>
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<tr>
<td>94.2</td>
<td>2982</td>
<td>56</td>
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<td>850</td>
</tr>
</tbody>
</table>

Run 142: 19.7% (19.7%) burn-off, 0.1205 g sample, CO₂/CO = 1.8

Run 156: 16.9% (16.9%) burn-off, 0.2718 g of sample, CO₂/CO = 1.4

Run 164A: 20.4% (0.4%) burn-off, 0.2467 g sample. CO₂/CO = 0.9

References