Effect of Small Concentrations of CO on Rate of Gasification of Spectroscopic Graphite in O_2

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Introduction

In CO_2 gasification of carbon, reactions (1) to (3), CO inhibits via reaction (2).[1]

$$C + CO_2 \rightarrow C(O) + CO \quad (1)$$
$$C(O) + CO \rightarrow CO_2 + C \quad (2)$$
$$C(O) \rightarrow CO \quad (3)$$

Reactions (2) and (3) are common to O_2 gasification of carbon. Although reaction (2) alters the CO_2/CO product ratio during steady state O_2 gasification of carbon[2], CO inhibition of O_2 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 O_2 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 CO_2 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 O_2 (>99.99%) with a H_2O <3 ppm, and a CO/CO_2/air mixture which had the CO_2 and H_2O 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 O_2 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 O_2 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 CO_2/CO ratio with no added CO and the average weight. Runs in Ar/O_2, with no added CO, showed that the product outlet concentrations were essentially unchanged as the inlet O_2 concentrations were varied over the small ranges given in Table 1. Blank runs with no graphite in the tray showed that ~8% 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 CO_2/CO ratios. This indicates catalytic influence, intrinsic[4] and/or extrinsic[5].

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 O_2 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 $C-O_2$ 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.

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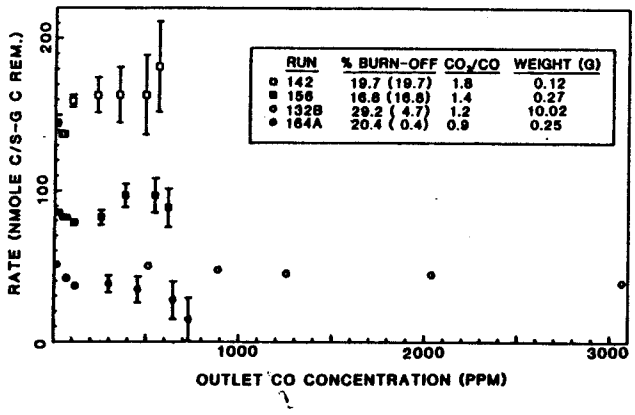

Figure 1. Effect of CO on Reactivity of Various Graphite Samples.

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References

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Table 1. Effects of CO Addition During Graphite Gasification in O_2

Oxygen Conc. (%)	Inlet Conc. CO (ppm)	Inlet Conc. CO_2 (ppm)	Outlet Conc. CO (ppm)	Outlet Conc. CO_2 (ppm)	Net. Conc. CO (ppm)	Net. Conc. CO_2 (ppm)	Net. Conc. C (ppm)	Net. Conc. O (ppm)	CO Oxidized (%)
Run 132B: 29.2% (4.7%) burn-off, 10.02 g sample, CO_2/CO = 1.2									
100.0	0	0	512	608	512	608	1120	1728	
99.0	492	13	887	682	395	669	1064	1733	
98.1	956	25	1255	737	299	712	1011	1723	
96.2	1828	43	2035	830	207	787	994	1781	
94.2	2982	56	3064	850	82	794	876	1670	
Run 142: 19.7% (19.7%) burn-off, 0.1205 g sample, CO_2/CO = 1.8									
100.0	0	0	14	25	14	25	39	64	
99.5	33	0	36	34	3	34	37	71	
99.0	59	1	55	42	-4	41	37	78	
98.0	111	2	94	62	-17	60	43	103	
94.3	310	5	230	129	-80	124	44	168	25.8
90.5	491	7	350	192	-141	185	44	229	28.7
86.7	703	9	492	263	-211	255	44	299	30.0
84.8	800	9	563	295	-237	286	49	335	29.6
Run 156: 16.9% (16.9%) burn-off, 0.2718 g of sample, CO_2/CO = 1.4									
100.0	0	0	22	30	22	30	52	82	
99.5	31	1	44	37	13	37	50	87	
99.0	59	1	65	45	6	44	50	94	
98.0	112	2	104	58	-8	56	48	104	
94.3	309	5	253	112	-57	107	50	158	18.4
90.5	481	7	385	162	-95	154	59	213	19.7
86.7	693	9	546	215	-147	206	59	265	21.2
84.8	782	10	617	229	-165	220	54	274	21.1
Run 164A: 20.4% (0.4%) burn-off, 0.2467 g sample. CO_2/CO = 0.9									
100.0	0	0	14	13	14	13	28	41	
99.0	60	1	67	18	7	16	23	39	
98.0	113	3	115	22	1	19	20	39	
94.3	309	5	297	39	-13	34	21	55	4.2
90.7	482	7	455	52	-26	45	19	64	5.4
86.6	689	9	646	67	-43	58	15	73	6.2
84.9	786	10	729	74	-57	65	8	73	7.2