EFFECT OF SMALL CONCENTRATIONS OF CO ON RATE OF GASIFICATION OF SPECTROSCOPIC GRAPHITE IN O_2

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Abstract—The influence of CO on the steady state gasification rate of a spectroscopically pure graphite powder with ultra high purity O_2 was studied at 840 ± 3 K for CO levels up to about 3000 ppm. The behavior of low reactivity samples differed from that of high reactivity samples. The gasification rate of low reactivity samples, distinguished as those having higher CO/CO_2 product ratios and lower gasification rates with no added CO, was inhibited by CO beyond that expected from simple dilution. The gasification of high reactivity samples was inhibited for CO additions under about 100 ppm. For higher CO additions, the gasification rate of high reactivity samples was unaffected or slightly enhanced. The difference in behavior is thought to be due to different, trace amounts of impurities (catalysts) present and the inability of these trace levels of catalysts to dissipate effectively the heat of CO oxidation. Accessible catalysts are thought to originate, more or less, from dust particles and impurities within the graphite.

1. INTRODUCTION

In the accepted mechanism for CO_2 gasification of carbon, reactions (1)–(3), CO acts as an inhibitor through reaction (2)[1].

$$CO_2 + C \longrightarrow C(O) + CO \qquad (1)$$

$$C(O) + CO \longrightarrow CO_2 + C \qquad (2)$$

$$C(O) \longrightarrow CO \qquad (3)$$
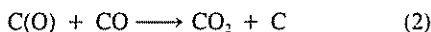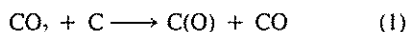
In reaction (2), the concentration of the desorbable intermediate surface oxide, C(O), is lowered without the removal of any lattice carbon. The rapidity of reaction (2) relative to the gasification step, reaction (3), at lower temperatures is responsible for the slow rate of CO_2 gasification under these conditions. Reactions (2) and (3) are also common to O_2 gasification of carbon. Although reaction (2) has been credited with the alteration of the CO/CO_2 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[3], the possibility of CO inhibition was raised. Therefore, it was of interest to explore the conditions under which CO inhibition may be found for O_2 gasification of carbon.

2. EXPERIMENTAL

2.1 Graphite

The carbon used was spectroscopic purity natural graphite powder, SP-1, produced by Union Carbide Corporation. It is comprised of flakes having diameters in the range 1–200 μm. The BET surface area (Kr, 0.195 nm^2, 77 K) is 1.8 m^2/g. Typical flake diameter and thickness are 30 μm and 0.5 μm, respectively. Microscopic examinations of the powder after various periods of oxidation reveal very few crystallite boundaries within the flakes and negligible basal plane pitting. The flakes do, however, exhibit extensive terracing in the basal plane. Estimates for the active area, (10 ℓ) and (11 ℓ) type planes, range from 3% of the total area (based on simple unroughened average geometry) to 30% of the total area (based on the Thomy and Duval method[3,4]). Total impurity content of the graphite is guaranteed to be under 1 ppm. The only impurities detected in the lot used were 0.1 ppm Fe, 0.1 ppm Mg and 0.2 ppm Si.

2.2 Gases

Ultra high purity Ar and ultra high purity, hydrocarbon free O_2 were obtained from Union Carbide Corporation, Linde Division. The Ar was further purified by a "Go Getter" gettering furnace made by General Electric Corporation to further reduce O_2 and H_2O levels to under 0.1 ppm. The O_2 was used as received. It has <3 ppm H_2O, <0.5 ppm total hydrocarbons, and >99.99% O_2. Carbon monoxide was obtained from a Matheson Company custom calibration mixture of CO and CO_2 in air. The CO_2 was removed by a proprietary adsorption tower which also contained anhydrous $CaSO_4$. This desiccant is capable of achieving H_2O levels of 7 ppm. The CO/air mixtures comprised less than 10% of the total gas flow.

2.3 Sample Preparation

The sample was used as received. It was poured directly into a sample boat of high purity alumina (>99.99% from Coors Porcelain Company or Morganite Refractory Company) or semiconductor grade quartz (Quartz Sci-

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entific Incorporated), heated for 4 h at 1234 K in a flow of Ar, cooled to reaction temperature, and then reacted with ~0.1 MPa O_2 at 840 ± 3 K. The gasification proceeded through three stages as noted by other workers[5]. Stage one is characterized by an initial high transient reaction which consumes about 0.002% of the sample. Stage one is observed whenever the graphite has been outgassed at high temperature. Stage two is characterized by a continually increasing gasification rate from 0% to about 2% burn-off. Stage two is only observed for previously unburnt samples. Stage three is characterized by a relatively constant gasification rate. During stage three, the gasification rate gradually increases with burn-off up to at least 20%. The increase in gasification rate with burn-off is more marked for smaller sample sizes but rapidly reaches a limiting value for sample sizes over 1 g.

Samples used for the CO addition experiments were all in stage three and all had been burnt-off to about 20%. Some of these samples were used without further treatment. Others were heat treated in Ar to 1234 K as done initially and then burnt-off an additional amount before use. Samples not given the extra heat treatment in Ar had higher reactivities and lower CO/CO_2 product ratios than those given the extra Ar heat treatment.

2.4 Apparatus

The same flow reactor was used for the Ar heat treatment, O_2 gasification, and CO addition experiments. Once the sample was loaded into the reactor, it was not exposed to the atmosphere until the CO addition experiments were completed. Apparatus details are given elsewhere [3]. Basically, the apparatus consists of a gas mixing system, a furnace, and a monitoring system for pressure, flow rate, CO concentration and CO_2 concentration. Product gas concentrations are determined by nondispersive infrared analyzers. Flow rate is determined by a thermal type mass flowmeter. Pressure is determined by a strain gauge type pressure transducer. The furnace has three independent heat zones and is double jacketed. A flowing ultra high purity Ar atmosphere is maintained between the jackets. The sample is contained in a boat in the center heat zone. A microcomputer controls the furnace temperatures and records the data. Instantaneous gasification rates are determined from the total gas flow and the product concentrations. Instantaneous sample weight is calculated from the initial weight and the integrated gasification rate. Calculated final sample weights agreed with gravimetrically determined final sample weights to within 0.5%. Inlet gases are blended to the desired concentrations with rotameters. The actual inlet gas concentrations are determined by the infra-red analyzers. The actual concentrations were in excellent agreement with concentrations calculated from the input gas concentrations and flows.

Calculations show that at reaction conditions used (~840 K, ~0.1 MPa O_2) negligible concentration gradients of O_2 existed through the graphite bed[3]. Further, the temperature difference between the bed and thermocouple located in the flowing gas above the bed was small[3].

2.5 Procedure

After the desired sample pretreatment had been given, the CO addition experiments were performed. For most of these experiments, the reactivity in pure O_2 at a set flow rate was determined before and after the CO addition experiment to check for changes in surface activity. Each CO addition experiment consisted of adding various amounts of CO to the O_2 inlet stream and monitoring the gasification rate. A comparative series of Ar additions, having matching O_2 concentrations, was performed at about the same time, usually just before the CO additions, to test for simple diluent effects. For both the CO and Ar additions, the total gas flow rate was kept constant at 0.6 L/min (STP). This value was chosen because the CO/CO_2 ratio for the pure O_2 reaction changes little with flow rate for flow rates over about 0.5 L/min. All runs were performed at a total pressure of 0.1 MPa. The furnace outlet concentrations were monitored for from 6 to 55 nominal residence times. Typically, 10 residence times were used. Steady state values were always obtained in less than 2 residence times. One nominal residence time, estimated by dividing the detector volume plus furnace volume by the gas flow rate, is about 1 min. Details of the procedure are given elsewhere [3].

3. RESULTS

The impetus for this study on the effect of CO on graphite gasification in O_2 was provided by our initial studies on the relationship between gasification rate and starting weight of graphite held in the sample boat. As is seen from the results, summarized in Fig. 1, large sample weights, over 1 g, showed a small decrease in reactivity with increase in weight; whereas, small sample weights, under 1 g, showed a large decrease in reactivity with increase in weight. In these runs, no CO was added to the inlet O_2. Since we were assured from our calculations[3] that temperature and gas concentration gradients down through the graphite beds were negligible, the effect of CO concentration in the bed, which did vary with bed weight, became of interest to us.

In order to determine whether the events of Ar addition, CO addition, or both together had any permanent effect on the carbon surface, gasification rates in 100% O_2 were measured before and after these events. For each kind of event, Table 1 tabulates exit CO concentration in the reactor, the gasification rate for reaction in pure O_2 for the time immediately preceding the event and for the time after the event when the pre-event conditions have been restored, the duration of the event, and the difference in rates in pure O_2 before and after the event. Throughout the paper, gasification rates are normalized by dividing the nmole of carbon gasified per second by the grams of carbon remaining to be gasified. The rate difference may be compared to that expected based on the previous rate versus time history. Low level additions of CO, less than 1000 ppm, which were used in runs 142 and 164A, do not affect the rates beyond that normally expected from the prior rate history. Higher level additions, greater than 1000 ppm, which were used in run 132B, decrease the rate below that expected from the prior rate history.
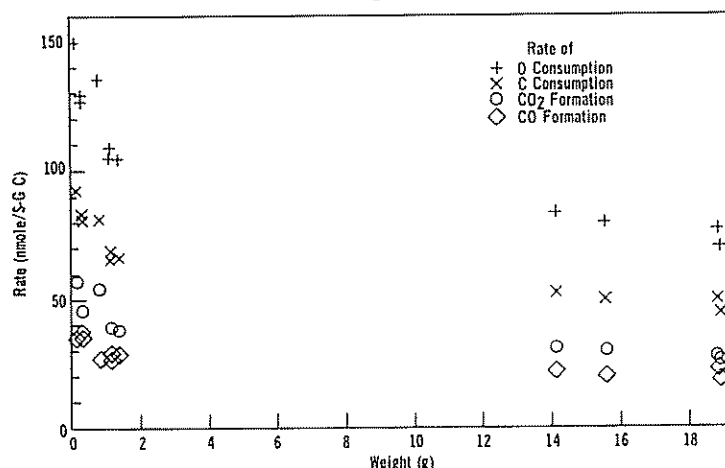
Fig. 1. Effect of initial graphite weight on reactivity at 10% carbon burn-off.

Table 2 presents results for a blank run in which the carbon sample was absent. The values under net concentration of carbon indicate the overall accuracy of the experiment. These values appear random and are within the experimental mixing accuracies. Table 2 shows that about 8% of the incoming CO in a $CO-O_2$ mixture is oxidized upon passage through the furnace at 0.6 L/min, independent of the CO concentration in the incoming stream.

Table 3 presents the results for CO additions to the O_2. Two burn-off values are given for each run. The first value is the total burn-off based on the as-received sample. The value in parentheses is the amount of burn-off since the most recent heat treatment. The sample weight listed for each run is the average weight during the CO addition experiment. The maximum burn-off which occurred during any of these experiments was in run 142 and was <4%. Runs in $Ar-O_2$ mixtures, with no CO added, showed that the outlet concentrations of CO and CO_2 were essentially unchanged as the inlet O_2 concentration was varied over the relatively small ranges given in Table 3 for the different graphite samples. That is, the diluent effect on reactivity was small under the conditions used.

Figure 2 presents the results of all the CO addition experiments as a plot of carbon gasification rates versus outlet CO concentration. The outlet CO concentration results from CO coming from carbon gasification and from CO added to the inlet O_2. The leftmost data point for each experiment is for no added CO. The variation in these gasification rates is due to different sample weights and different amounts of burn-off since the last heat treatment, as will be discussed shortly. Error bars indicate the range in values expected from errors in mixing the gases. Errors for run 132B are less than the symbol size and are, therefore, not shown in Fig. 2.

4. DISCUSSION

Before considering the effect of CO addition on the rate of gasification of spectroscopic graphite in O_2 at 840 K, one should consider the complications introduced by observing different gasification rates for the four runs at fixed levels of CO concentration, as seen in Fig. 2. In some cases, gasification rates differing by as much as a factor of four are observed at fixed levels of CO concentration. Run 142, which showed the highest reactivity at all levels of CO concentration, used the smallest weight

Table 1. Effect of CO and/or Ar additions (event) on subsequent gasification rates in pure O_2

Run	BEFORE EVENT		AFTER EVENT		Event Duration (h)	Rate Change (nmoles C s-g C)	Expected Rate Change [1] (nmoles C s-g C)
	CO Concentration (ppm)	Rate (nmoles C s-g C)	CO Concentration (ppm)	Rate (nmoles C s-g C)			
			Event: Ar Addition to O_2				
142	12	137.3	14	142.8	0.67	5.5	1.0
156	22	84.5	22	84.6	1.00	0.1	0.4
			Event: CO Addition to O_2				
142	13	142.8	15	154.0	6.70	11.2	9.6
164A	13	46.2	14	48.4	3.38	2.2	1.6
		Event: Ar Addition to O_2 and CO Addition to O_2					
132B	522	50.2	510	44.4	5.16	-5.8	0.0

[1]Rate change obtained from slope of rate versus time prior to the event.

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Table 2. Extent of CO oxidation in absence of graphite sample

O_2 Conc. (%)	Inlet Conc.		Outlet Conc.		Net Conc.				CO Oxidized (%)
	CO (ppm)	CO_2 (ppm)	CO (ppm)	CO_2 (ppm)	CO (ppm)	CO_2 (ppm)	C (ppm)	O ppm	
100.00	0.3	0.0	0.1	0.2	−0.2	0.2	0.0	0.2	**
99.47	29.6	0.6	25.8	2.1	−3.8	1.5	−2.3	−0.8	12.8
98.99	56.9	1.1	53.5	4.6	−3.4	3.5	0.1	3.6	6.0
98.02	107.2	2.1	99.4	9.6	−7.8	7.5	−0.3	7.2	7.3
94.32	311.1	5.1	289.4	28.0	−21.7	22.9	1.2	24.1	7.0
90.50	488.9	7.0	447.7	44.0	−41.2	37.0	−4.2	32.8	8.4
86.70	690.7	8.6	635.9	64.2	−54.8	55.6	0.8	56.4	7.9
84.77	781.4	9.2	720.8	72.6	−60.6	63.4	2.8	66.2	7.8

**
not significant

of graphite in the boat and was conducted following the largest amount of carbon burn-off at 840 K after heat treatment in 0.1 MPa Ar at 1234 K. By contrast, run 164A, which showed the lowest reactivity at all levels of CO concentration, used an intermediate weight of graphite in the boat and was conducted following the smallest amount of carbon burn-off at 840 K after heat treatment.

Table 4 summarizes data for reactivity and product CO/CO_2 ratios when no CO was added to the incoming O_2 stream. Run 142, which exhibited the highest reactivity, has the lowest CO/CO_2 ratio; runs 132B and 164A, which exhibited the lowest reactivities, have the highest CO/CO_2 ratios. Many workers have been concerned with the product CO/CO_2 ratio as a result of gasification of

high purity graphites in O_2. Heuchamps et al. reacted very high purity graphite in 0.1 MPa of very dry air at 903 K[6]. The product CO/CO_2 ratio decreased continuously with increasing amount of carbon gasified from 1.3 at 10% burn-off to 0.11 at 98% burn-off. The authors attribute the decrease in CO/CO_2 ratio with increasing burn-off to a concurrent increase in amount of impurities on the graphite surface. They suggest that overall gasification rates are the sum of an uncatalyzed gasification rate, where O_2 dissociates at carbon active sites, and a catalyzed gasification rate, where O_2 first dissociates at catalytic active sites[7]. For the uncatalyzed reaction, CO is the main primary product; for the catalyzed reaction CO_2 is the main primary product. Impurites also catalyze the secondary oxidation of CO to CO_2. Thus it was also

Table 3. Effects of CO addition during graphite gasification in O_2

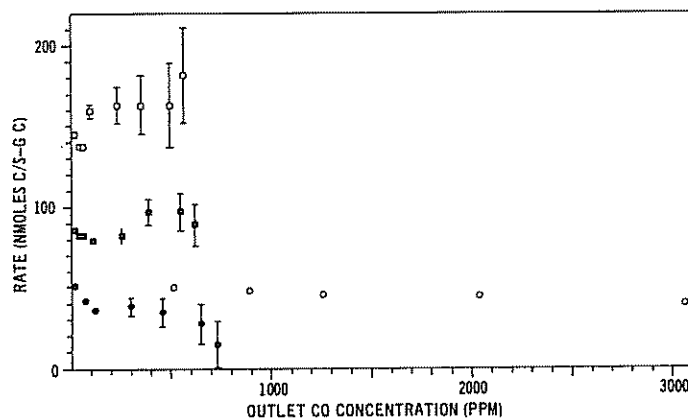| Oxygen Conc. (%)	Inlet Conc.		Outlet Conc.		Net Conc.			
	CO (ppm)	CO_2 (ppm)	CO (ppm)	CO_2 (ppm)	CO (ppm)	CO_2 (ppm)	C (ppm)	O (ppm)
Run 132B, Conditions: 29.2% (4.7%) burn-off, 10.02 g sample								
100.0	0	0	512	608	512	608	1120	1728
99.0	492	13	887	682	395	669	1064	1733
98.1	956	25	1255	737	299	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, Conditions: 19.7% (19.7%) burn-off; 0.1205 g sample								
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
90.5	491	7	350	192	−141	185	44	229
86.7	703	9	492	263	−211	255	44	299
84.8	800	9	563	295	−237	286	49	335
Run 156, Conditions: 16.9% (16.9%) burn-off, 0.2718 g sample								
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
90.5	481	7	385	162	−95	154	59	213
86.7	693	9	546	215	−147	206	59	265
84.8	782	10	617	229	−165	220	54	274
Run 164A, Conditions: 20.4% (0.4%) burn-off, 0.2467 g sample								
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
90.7	482	7	455	52	−26	45	19	64
86.6	689	9	646	67	−43	58	15	73
84.9	786	10	729	74	−57	65	8	73

Fig. 2. Effect of CO on reactivity of various samples: O, 132B; □, 142; ▓, 156; ◉, 164A. Important conditions for these runs are given in Table 3.

found that as the gasification rate of a high purity graphite to which varying amounts of Na and K were added increased, the product CO/CO_2 ratio decreased[7].

It is, therefore, concluded that differences in reactivity and CO/CO_2 ratios found in this study can be attributed, primarily, to differences in amount and specific activity of accessible impurities. Intrinsic impurities, located along crystallite boundaries, are made accessible upon gasification and enlargement of the boundaries. Extrinsic impurities are derived from dust particles which contaminate the graphite and boat upon exposure to air prior to loading the sample into the reactor. Such contamination was previously found to catalyze oxygen isotopic exchange in CO_2 [reactions (1) and (2)] at 773 K in the presence of a high purity quartz sample boat[8]. Activity of the boat could be sharply reduced by heating in air in the reactor at 1173 K prior to making an activity run. However, subsequent removal of the boat from the reactor for a very short period of time increased its activity by two orders of magnitude. The graphite sample in run 142 (which had the highest reactivity) would be expected to have the highest level of accessible impurities for two reasons. First, in run 142 the smallest weight of graphite was used; this would result in extrinsic impurities making the greatest contribution to total impurity content. Scanning electron micrographs of graphite flakes following gasification confirmed that samples where the starting weight of graphite was low were more severely channeled and roughened than were samples of large starting weights. Such channeling and roughening is indicative of catalyzed carbon gasification. Second, the graphite had undergone the greatest burn-off since the last heat treatment at 1234 K. It is thought that such heat treatment would decrease the contribution of catalyzed gasification

to overall gasification as total impurity content decreases because of some volatilization and as the dispersion of remaining impurities decreases due to sintering. Run 164A shows the important effect which heat treatment at 1234 K has on subsequent reactivity at 840 K. Even though the sample weight used was not large (0.25 g), the graphite had undergone only 0.4% burn-off since heat treatment; this sample had the lowest reactivity.

Intrinsic impurities in the high purity alumina or quartz boats appeared to have little effect on graphite reactivity, since reactivity was essentially independent of boat material. Further, addition of high purity alumina powder to the graphite, such that contact area between graphite and alumina was increased about 37 times, had no marked effect on gasification rate.

The apparent presence of variable amounts and activities of impurities in this study makes interpretation of the effect of CO on the gasification rate of graphite in O_2 more difficult. Consider that the overall gasification rate is the sum of an uncatalyzed rate and a catalyzed rate. It is clear that the uncatalyzed rate of carbon gasification in O_2 will be inhibited by product CO or CO added to the inlet gas stream to the extent that reaction (2) competes with reaction (3). The effect of CO on the rate of the catalyzed reaction is not as clear. Impurities are thought to be catalysts for carbon gasification in O_2 primarily because they are more efficient at dissociating O_2 upon its collision with their surface than upon its collision with the carbon surface. Following dissociation of O_2 into atomic oxygen, gasification is expected to be rapid once the atomic oxygen reaches a carbon active site. Carbon monoxide can inhibit this process in at least three ways. One, it can react with atomic oxygen before it leaves the impurity site, producing CO_2. Two, it can

Table 4. Gasification rates and product CO/CO_2 ratios with no CO added to incoming O_2

Run	Rate nmoles C/s-g C	CO/CO_2
132B	50	0.84
142	144	0.56
156	85	0.74
164A	51	1.08

intercept the oxygen atom as it diffuses across the carbon surface to an active carbon site, again producing CO_2. Three, it can compete with O_2 for free sites on the impurity surface by chemisorption and thereby reduce the probability that O_2 will dissociate upon collision with the surface. On the other hand, CO can also accelerate catalyzed gasification of carbon in O_2. Impurities which dissociate O_2 catalyze the oxidation of CO to CO_2, a highly exothermic reaction. As the rate of this reaction increases, impurity particles are heated to higher temperatures. In turn, since the impurity surface is at a higher temperature the rate of dissociation of O_2 is increased, which can lead to a more rapid rate of atomic oxygen leaving impurity sites and gasifying carbon. The optimum CO/O_2 ratio for the maximum rate of CO oxidation to CO_2 over impurity sites depends upon the extent to which CO and O_2 compete for (or cover) particular impurity sites[9].

Proof that catalysis of CO oxidation over impurity sites occurred at a significant rate can be obtained from data in Tables 2 and 3. As noted earlier, in the absence of a graphite sample, ~8% of the CO in all incoming CO–O_2 mixtures was oxidized to CO_2 at 840 K. Compare this result with results for runs in which a graphite sample was held in the boat and ~480 ppm CO were present in the incoming stream. In runs 142 and 156, which showed the highest graphite gasification rates, the concentration of outgoing CO was 29 and 20% lower, respectively, than the inlet CO concentration. That is, the reduction in CO concentration was greater than that found in the absence of a graphite sample in spite of the fact that graphite was being gasified by O_2 to produce some CO. This means that most oxygen atoms produced by O_2 dissociation at impurity sites were, in turn, consumed by CO producing CO_2 rather than migrating to an active carbon site and producing CO. The impurities were more efficient oxidation catalysts for CO than gasification catalysts for carbon producing CO in the presence of O_2. Only for run 132B, where there was a large weight of graphite used, was there a net production of CO found. In this case, the rate of uncatalyzed carbon gasification producing CO exceeded the rate of oxidation of CO at impurity sites.

Consider now the effect of CO on rates of graphite gasification in O_2. Results presented in Fig. 2 show that for very low levels of CO, carbon gasification is inhibited to an increasing extent as the CO concentration is increased. For runs 142 and 156, which are thought to contain the greatest concentration of impurities, gasifi-

cation rates clearly go through a minimum with further additions of CO before leveling off at higher rates. For run 164A, with a lower concentration of impurities, the minimum is very shallow, followed by decreasing gasification rates with increasing CO concentrations. For run 132B, where a large sample weight of graphite was used, large increases in CO concentration from 500 to about 3000 ppm resulted in a gradual decrease in gasification rate up to 28%. This is significantly greater than would be found by simple dilution of the O_2 stream (for example, by Ar). Thus results shown in Fig. 2 reflect all the complexities of possible inhibition and acceleration of graphite gasification in O_2 by CO just discussed.

5. CONCLUSIONS

Carbon monoxide inhibition of the steady state C–O_2 reaction at 840 K (in the absence of diffusional effects) is found when the rate of carbon gasification is thought to be dominated by the uncatalyzed reaction. This is the case when large weights of graphite are used and/or the sample has been heated to an elevated temperature in the reactor (~1200 K) before much additional carbon burnoff has ensued. When the rate of catalyzed gasification becomes a significant part of the overall rate, the effect of CO is complicated by catalysis of CO oxidation to CO_2 at impurity sites. Such oxidation can heat up impurity sites and result in their becoming more efficient at dissociating O_2. This can lead to higher carbon gasification rates.

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