

NOTES

The Effects of Particulate Oxides of the Group IIIB Elements on Oxidation Rates of Graphite in Air

The majority of metal oxides which exhibit catalytic activity in promoting the reaction of carbon with gaseous molecular oxygen are capable of undergoing cyclic redox processes on the carbon surface during the gasification reaction (1, 2). In most cases, the catalytic effect can be explained satisfactorily by the occurrence of sequential reactions in which the mobile catalyst particles are reduced to a lower oxidation state by reaction with the carbon substrate and are subsequently converted back to the original state by oxidation with ambient oxygen. The net effect of this cyclic process is the gasification of carbon at the moving catalyst particle-carbon interface and the simultaneous formation of pits and/or channels in or beneath the carbon surface (3, 4). Catalytic activity is found with the oxides of a wide range of elements, but especially with those of Groups I, II, and the transition metals (2). In these cases, very small amounts (ppm) of catalytic impurity can have profound effects on the reactivity of carbonaceous materials in air or oxygen.

Oxides of the elements of Group IIIB are not generally considered to be active catalysts for this reaction. In fact, boron oxide is a strong inhibitor of carbon oxidation (5, 6) and has been used to protect carbon/carbon composites against oxidation in air to temperatures of 1000°C (7, 8). Aluminum also forms a very stable oxide which is not reduced by carbon except at temperatures exceeding 1700°C (9). Alumina has never been shown to be an active catalyst for carbon oxidation. It is in fact possible to predict the general catalytic behavior of metal oxides in this reaction from a consid-

eration of the free energies of their reactions with carbon as functions of temperature.

Figure 1 shows a plot of the free energy (ΔG°) vs temperature for the carbothermic reduction reaction $M_2O_3 + 3C = 2M + 3CO$ for oxides of the Group IIIB elements, using data for the free energies of formation available in the literature (10). The oxides of gallium, indium, and thallium have not hitherto been studied as catalysts for carbon oxidation but, on the basis of the free energies shown in Fig. 1 and under the assumption of the redox mechanism described above, it is predicted that gallium oxide would be inactive, indium oxide might show slight catalytic activity at high temperatures, and thallium oxide would be a very active catalyst for carbon oxidation at low temperatures. In order to test this prediction and the proposed redox mechanism for the catalysis process, the effect of additions of these three oxides on the kinetics of oxidation of graphite in air was studied.

Various concentrations of pure powdered gallium oxide Ga_2O_3 (Alfa Products Inc.), thallium oxide (Fisher Scientific Co.), indium hydroxide (City Chemical Corp.), and indium acetate (Alfa Products Inc) were added to 100-mg amounts of spectroscopic grade graphite powder (Type UCP-2, 100 mesh, Ultra Carbon Corp.) and the mixtures were blended in a Fisher Minimill to give carbon/oxide weight ratios ranging from 50/1 to 1/1. Measurements of the isothermal kinetics of the oxidation of these mixtures in dried flowing air (1 atm, 0.1 MPa) were carried out in a Mettler Thermoanalyzer TA-2 controlled-atmo-

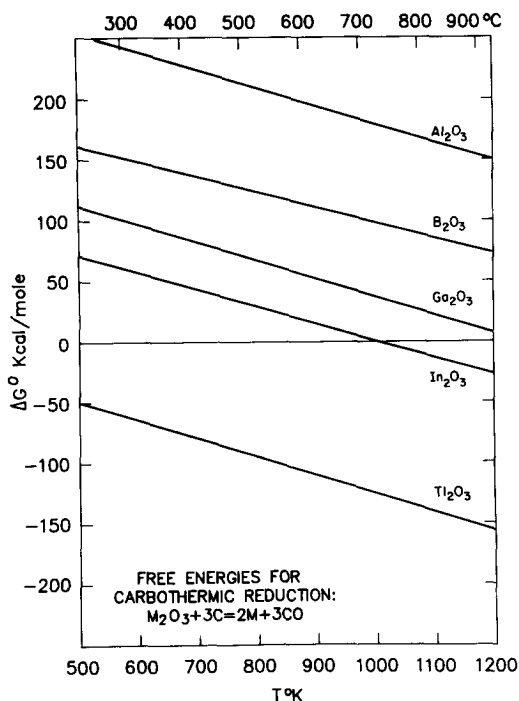


FIG. 1. Standard free energies (ΔG°) vs temperature for the carbothermic reduction of the oxides of Group IIIB elements.

sphere automatic thermobalance, using 100-mg samples and an air flow rate of 200 ml/min.

Figure 2 shows thermogravimetric data

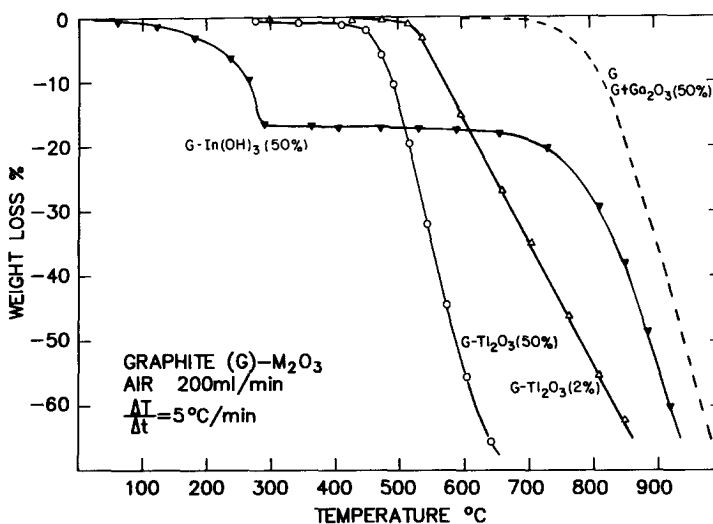


FIG. 2. Weight loss vs temperature thermograms for pure graphite (G), mixtures of graphite with equal weights of Ga_2O_3 and $\text{In}(\text{OH})_3$, and graphite doped with 2 and 50 wt% Tl_2O_3 , on heating in air.

obtained on heating pure graphite powder and graphite with added gallium oxide, thallium oxide, or indium hydroxide in flowing air at a linear heating rate of $5^\circ\text{C}/\text{min}$. The identical weight losses observed for pure graphite and graphite + 50% Ga_2O_3 are indicated by the dashed curve. Apparently the effects of this oxide on the kinetics of the graphite-oxygen reaction were negligible under the conditions of these experiments. Finely dispersed indium oxide, formed by the thermal decomposition of the hydroxide and acetate, had a small catalytic effect on the rate of gasification of the graphite above 700°C . In contrast, graphite samples doped with 2 and 50 wt% Tl_2O_3 showed greatly enhanced reactivity toward oxygen, with weight losses resulting from carbon gasification being observed at temperatures several hundred degrees lower than for pure graphite.

Insight into the reactions involved in the catalytic effect exhibited by thallium oxide is given by the thermogravimetric data shown in Fig. 3. This oxide is appreciably volatile at temperatures above 750°C , as shown by the dashed curve, obtained on heating 100 mg of the oxide in flowing air. A mixture of equal weights of graphite and Tl_2O_3 , on heating in flowing nitrogen, lost

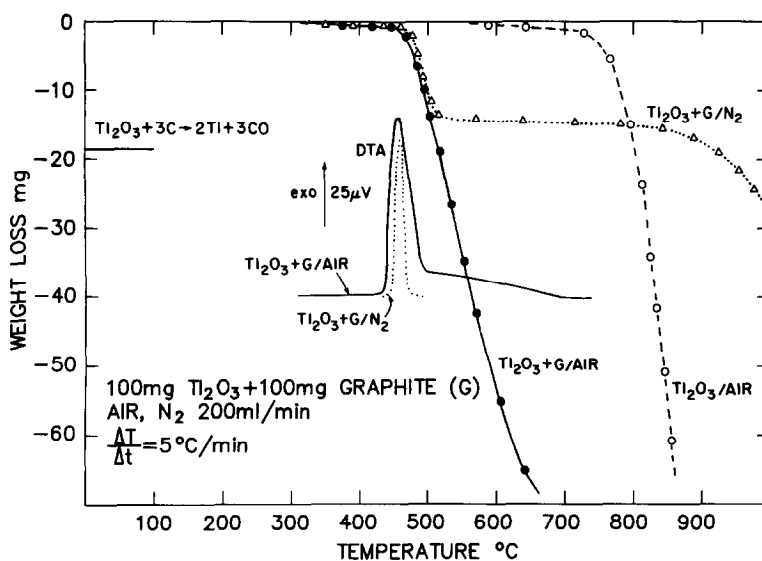


FIG. 3. TGA-DTA curves for Ti_2O_3 and graphite + Ti_2O_3 in air and nitrogen.

weight suddenly between 470 and 520°C as a result of the occurrence of the carbothermic reduction reaction $\text{Ti}_2\text{O}_3 + 3\text{C} = 2\text{Ti} + 3\text{CO}$, as shown by the dotted curve in Fig. 3. This reaction appeared to be essentially complete when a temperature of 600°C was reached. X-ray diffraction analysis of the product obtained after heating to 1000°C showed substantial amounts of metallic thallium and only trace quantities of residual thallium oxide. When a mixture of equal weights of graphite and Ti_2O_3 was heated in flowing air (solid curve, Fig. 3), weight losses began abruptly at about 470°C. In fact, the lower part of the weight loss vs temperature curve (470–500°C) coincided with that for the mixture heated in nitrogen (dotted curve, Fig. 3). Weight losses due to the catalyzed gasification of carbon became very rapid when the mixture was heated in air above 500°C. In fact, the rates of both the carbothermic reduction reaction and the graphite oxidation reaction were probably diffusion-controlled at 500°C, the former by the rate of carbon monoxide diffusion from the graphite surface, and the latter by the rate of diffusion of oxygen to the graphite surface. Both reactions were

strongly exothermic, as shown by the DTA peaks indicated in Fig. 3.

The labile intermediate in the catalytic redox cycle was thallium metal, which has a very low melting point (303.5°C) and hence tends to spread rapidly over the graphite surface, thereby enhancing the catalytic effect. Figure 4 shows Arrhenius plots for the oxidation in flowing air of pure graphite (dashed line) and for graphite doped with 2% Ti_2O_3 . In these experiments fresh samples of the doped graphite were used for each data point and the rates are given in terms of a rate constant, $K = \Delta W/W_0 \cdot t$, expressed in min^{-1} . It is clear that a very large catalytic effect was involved, with carbon gasification rates being increased by three orders of magnitude in the presence of 2 wt% thallium oxide. The catalyzed reaction was measurable even below 400°C, and at 500°C and above the rates became so large they were limited by the rates of diffusion of gaseous oxygen to the carbon surface (Zone III kinetics, (11)). It has been shown previously that low melting point phases may be particularly effective as carbon oxidation catalysts (12) and it is likely that in the present case the

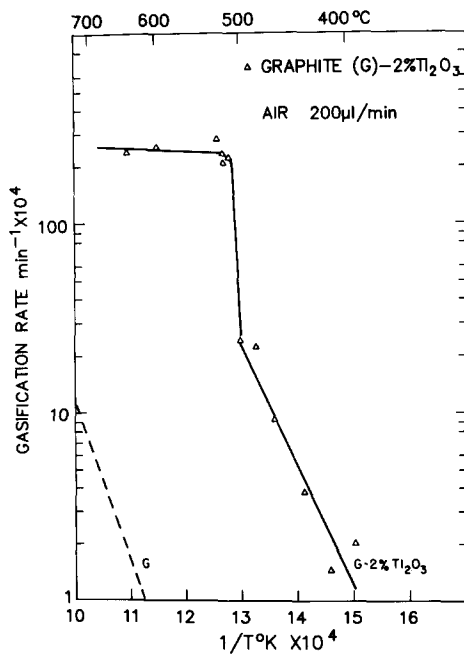


FIG. 4. Arrhenius plots (log gasification rate vs $1/T$) for pure graphite (G) and graphite doped with 2 wt% Ti_2O_3 .

mobility of the molten thallium droplets aided the dispersion of the catalytic material throughout the carbon substrate. Although, because of its toxicity, thallium oxide is unlikely to be a useful catalyst for carbon gasification, the catalytic effect has not been reported previously and the pre-

diction of the behavior on thermodynamic grounds adds support to the cyclic redox mechanism proposed for the catalytic process.

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