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Note

THORIUM AS A CARBON OXIDATION CATALYST

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A large number of metal oxides are known to catalyze the gasification of carbon by molecular oxygen [1,2] and very small concentrations of the most active materials are capable of reducing the temperature at which carbon begins to oxidize in air by several hundred degrees [3]. Although active catalytic species come from every Group of the Periodic Table, the majority of catalysts appear to function via a redox cycle, being reduced to lower oxidation states by reaction with the carbon substrate and then reoxidizing back to the original state by reaction with ambient oxygen [3,4]. A few catalysts, such as Cr_2O_3, silver metal and possibly transition metal carbides [5], appear to accelerate the oxidation reaction by providing sites for the dissociation of molecular oxygen to give absorbed oxygen atoms, which then diffuse across the carbon surface to active sites where the carbon is gasified. In some cases the catalytic effect may be enhanced by the formation of a molten phase, followed by spreading and wetting of the carbon surface [6].

The actinide elements and their compounds have not been studied as catalysts for this reaction, although their behavior is somewhat predictable based on the above considerations. Uranium, which forms a series of oxides, has been found to be active catalytically, when present as UO_3 or U_3O_8 [7]. Sampath et al. [8] have, however, recently reported that thorium oxide, ThO_2, is an active catalyst for the oxidation of graphite in air in the temperature range 600–900°C. As the single oxide of thorium is very stable ($\Delta H^0_{298} = -293$ kcal mol^{-1}), it would not be reduced to metal by heating with carbon in this temperature range and hence it would not be expected to participate in oxidation–reduction cycles on the graphite surface. ThO_2 is also much more stable in the presence of oxygen than the known carbides, ThC and ThC_2, and hence carbide formation during carbon gasification would not be expected. In addition, the very high melting point (3220°C) of ThO_2 would preclude the formation of molten phases and the wetting of the graphite substrate. For all these reasons a demonstrated catalytic activity for thoria would disqualify the usual redox process as the likely mechanism of the catalyzed gasification of carbon in this case, and as ThO_2 is only an indifferent catalyst for gas phase oxidation reactions (e.g., oxidation of CO) [9], it is also improbable that this oxide would bring about the dissociation

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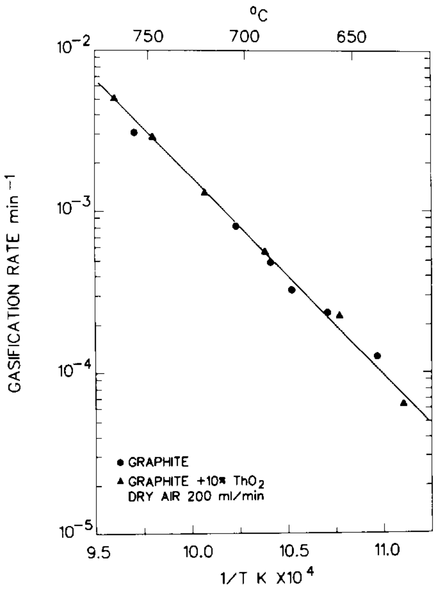

Fig. 1. Kinetic data for oxidation of graphite and graphite +10% ThO_2 in air. Log gasification rates vs. $1/T$.

of O_2 to any significant extent. It is therefore clear that a confirmed strong catalytic activity for thoria in the carbon gasification reaction would have important mechanistic implications.

Thermogravimetric measurements of the oxidation kinetics of graphite powder in flowing air, in the presence and absence of added thoria, were made in a Mettler Thermoanalyzer TA-2 controlled-atmosphere balance. The spectroscopic grade graphite (UCP-2 100 mesh, 2.3 m^2 g^{-1} surface area initially) was obtained from Ultra Carbon Corporation. The thoria was Fisher Scientific Company C.P. Grade ThO_2. Weight loss measurements were made in dried flowing air (200 ml min^{-1}) with a linear furnace heating rate of 5°C min^{-1} and also isothermally in the temperature range 600–800°C.

Figure 1 shows Arrhenius plots (log gasification rate, $\Delta W/W_0$ vs. $1/T$ (K)) for the gasification of pure graphite and graphite with 10 wt.% of added and intimately mixed ThO_2. It is clear that kinetic data for both pure and doped graphite samples lie on the same line, the slope of which gives an apparent activation energy of 56 ± 1 kcal mol^{-1} for the oxidation reaction. Figure 2 shows thermogravimetric data obtained on heating pure graphite powder and graphite mixed with an equal weight of ThO_2 in flowing air at a constant linear heating rate. The identical weight loss vs. temperature curves for the two samples indicate that the effect of the ThO_2 on the kinetics of the graphite–oxygen reaction is negligible under the conditions of these experiments. The results reported by Sampath et al. are therefore unex-

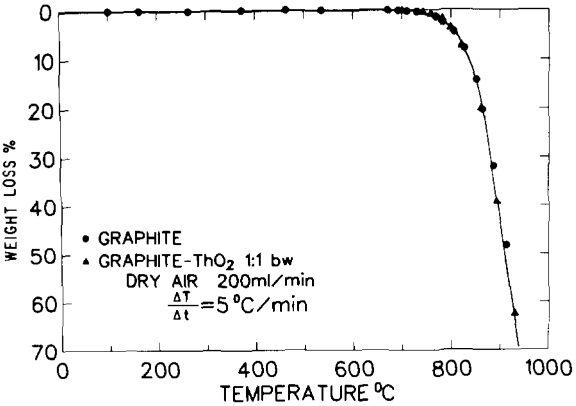

Fig. 2. Weight loss vs. temperature thermograms for pure graphite and a 1 : 1 mixture of graphite and ThO_2 in flowing air. Heating rate = 5 °C min^{-1}.

plained, although it is possible that thoria obtained from the ore monazite, a complex phosphate containing uranium, cerium and other lanthanides [10], may obtain traces of these impurities which are known to be active catalysts for carbon oxidation [11].

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