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The Catalytic Effects of Uranium Oxides and Salts in Carbon Oxidation

The gasification reactions of carbon belong to an unusual class of heterogeneous processes involving the conversion of a solid phase into gaseous products. These reactions, which are of great technological importance, are catalyzed by many diverse types of inorganic species. In fact, active catalysts for carbon oxidation include members of every group in the Periodic Table (*1*, *2*). Although the detailed mechanism of few of these catalytic reactions have been unequivocally determined, it is generally agreed that cyclic redox processes on the carbon surface are probably the basis for the catalytic behavior (*3*, *4*). For example, active catalysts such as transition metal oxides may be reduced to a lower oxidation state by reaction with the carbon substrate at gasification temperatures and may then be reconverted back to the initial state by reaction with ambient oxygen (*5*, *6*). The net effect of this cyclic process would be the gasification of the carbon at the catalyst particle–substrate interface, a process which is often promoted by vigorous mobility of the catalyst particles over the carbon surface (*7*, *8*). The metal uranium, which forms a complex series of interconvertible oxides, has apparently not hitherto been investigated as a catalyst for carbon oxidation and hence would provide a useful test for the redox mechanism. Uranium oxide and uranyl compounds are known to be active catalysts for olefin oxidation (*9*, *10*). U–Sb-oxide catalysts have also been found to be active in the allylic oxidation of alkenes (*11*). Uranium is found as a minor element in many coals (*12*), so that an understanding of its catalytic behavior during coal combustion would be of technological interest. This note describes the results of a study of the behavior of a series of uranium oxides and uranyl salts as catalysts for the oxidation of graphite in air in the temperature range 500–1000°C.

Uranium dioxide, UO_2, was prepared by passing uranium hexafluoride, UF_6, into ammonium hydroxide solution to give a precipitate of "ammonium diuranate" $(NH_4)_2U_2O_7 \cdot xH_2O$, which was dried and then calcined at 450°C to form UO_3. Reduction to brown UO_2 was carried out by heating in flowing hydrogen at 700°C. Uranium peroxide, $UO_4 \cdot 2H_2O$, was prepared by reacting uranyl nitrate solution with 30% hydrogen peroxide solution to give a lemon-yellow precipitate which was filtered and dried. Uranium trioxide, UO_3, was prepared by heating the peroxide in air to 450°C to give the orange–red trioxide. The black oxide, U_3O_8, was made by heating the trioxide in air to 650°C. Reagent grade uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, was obtained from Alfa Inorganics, and uranyl acetate, $UO_2\,(acet)_2 \cdot 2H_2O$, from Matheson, Coleman and Bell. Spectroscopic Grade graphite powder (Ultra Carbon Corp., Type UCP-2, 100 mesh, 2.3 m^2/g surface area initially) was doped with known amounts of the finely powdered oxides and salts and the mixtures blended in a Fisher Minimill before the reactivity measurements. Kinetic measurements and thermogravimetry were carried out in a Mettler Thermoanalyzer TA-2 controlled-atmosphere balance.

Figure 1 shows a summary of weight loss vs temperature measurements for pure graphite (G) in air, a mixture of equal weights of graphite and uranyl nitrate in argon (A) and in air (B). Shown in curve (C)

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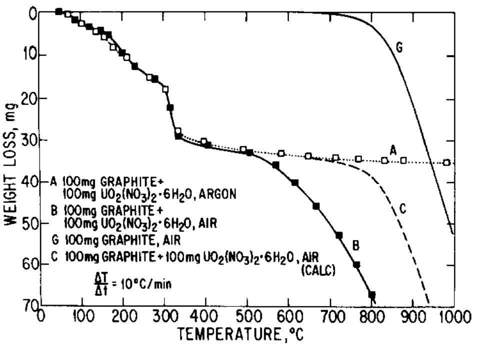

FIG. 1. Weight loss vs temperature thermograms for 100 mg pure graphite (G), and a mixture of 100 mg graphite + 100 mg uranyl nitrate in flowing argon (A) and air (B). Curve C shows calculated weight losses for a similar graphite–uranyl mixture in the absence of catalysis.

are the calculated weight losses for a mixture of equal weights of uranyl nitrate and graphite on heating in air, assuming no interaction between the two phases. Comparison of curves (B) and (C) indicates that, whereas pure graphite begins to gasify rapidly in air at temperatures exceeding 700°C, in the presence of the uranyl salt gasification begins at about 500°C. It is clear that the uranium compound, which decomposes to UO_3 above 400°C (*13*), is exerting a powerful catalytic effect on the graphite oxidation reaction.

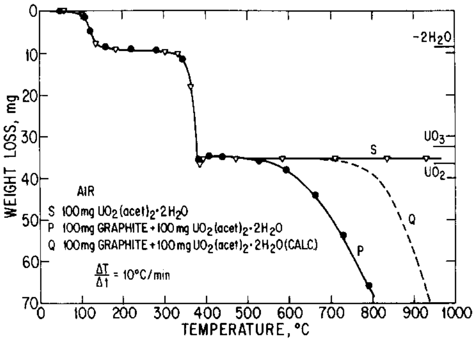

FIG. 2. Weight loss vs temperature thermograms for 100 mg uranyl acetate (S) and a mixture of 100 mg graphite + 100 mg uranyl acetate (P) in flowing air. Curve Q shows calculated weight losses for a similar graphite–uranyl acetate mixture in the absence of catalysis.

Thermogravimetric data obtained with uranyl acetate and mixtures of this salt with graphite on heating in air are shown in Fig. 2. The pure salt loses water of hydration below 200°C and then decomposes on further heating to give uranium oxide at 350–400°C. The measured weight loss suggests that a mixture of the oxides UO_2 and UO_3 is the product of this decomposition reaction (curve S). Curve P shows the measured weight losses on heating in air a mixture of equal weights of uranyl acetate and graphite. Comparison with the calculated curve Q, derived on the basis of no interaction between the two phases, indicates that uranyl acetate, or rather the uranium oxides derived therefrom, is a potent catalyst for graphite oxidation, the presence of the uranium phase resulting in a decrease in the gasification temperature by over 200°C.

Arrhenius plots (log rate vs $1/T$) for the gasification of a series of uranyl acetate-doped graphite samples in air are shown in Fig. 3, which includes comparison data for pure graphite under the same conditions. The catalytically active phase derived from uranyl acetate is even more effective than

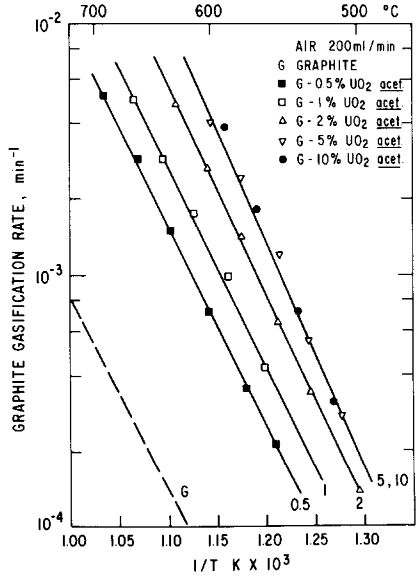

FIG. 3. Arrhenius plots (log gasification rate vs $1/T$) for pure graphite (G) and graphite doped with 0.5, 1, 2, 5, and 10 wt% uranyl acetate.

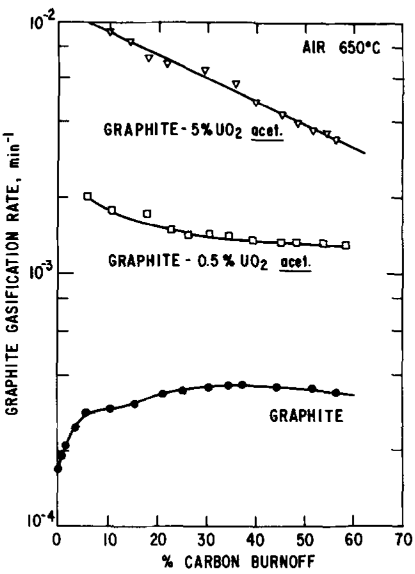

FIG. 4. Variation of carbon gasification rate for pure graphite and graphite doped with 0.5 and 5 wt% uranyl acetate as a function of carbon burnoff.

that derived from uranyl nitrate in promoting the oxidation of graphite. Thus as little as 0.5 wt% of the added salt accelerates the gasification reaction by about an order of magnitude. The measured rate increases with increasing catalyst concentration, but above 5 wt% there is no further increase. As with uranyl nitrate, the catalyst has little effect on the apparent activation energy of the gasification reaction, the main effect arising from increases in the preexponential factor in the Arrhenius equation, a parameter which reflects the number of active sites on the carbon surface. The effect of increasing burnoff on the rates of gasification in air at 650°C is illustrated in Fig. 4, for pure graphite and for two samples doped with uranyl acetate. With pure graphite a rise in gasification rate is initially observed, probably as a result of increasing surface area of the sample. Above about 5% burnoff, however, the gasification rate remains fairly constant. A similar variation of gasification rate with burnoff has been observed before for another type of pure graphite powder (*14*). On the other hand, the doped graphite samples exhibit a steady decline in reactivity with burnoff, the decrease being most marked for the sample containing the higher concentration of catalyst. This effect may be due to the progressive loss of contact of the catalyst phase with the graphite substrate as the latter burns away during the course of the reaction.

Thermogravimetric data for the oxide UO_3 mixed with an equal weight of graphite and heated in air or argon are shown in Fig. 5. Curve U indicates that UO_3–graphite mixtures lose a small amount of weight between 600 and 1000°C on heating in argon, as a result of partial reduction to the dioxide UO_2. In the presence of air (curve V), gasification of the graphite begins at about 650°C and, comparison with the calculated weight loss profile (curve W), indicates that a catalytic effect is again occurring. A comparison of the catalytic effects exhibited by the different uranium oxides (added at an initial concentration of 10 wt% to the graphite) is shown in Fig. 6, in the form of Arrhenius plots of log rate vs 1/temperature. The general order of catalytic activity is $U_3O_8 < UO_2 < UO_3 = UO_4$. As the peroxide UO_4 is completely converted to UO_3 and the lower oxides UO_2 and U_3O_8 are partially converted to UO_3 at temperatures in the gasification range, it seems likely that UO_3 is the active catalytic entity in each case. Also,

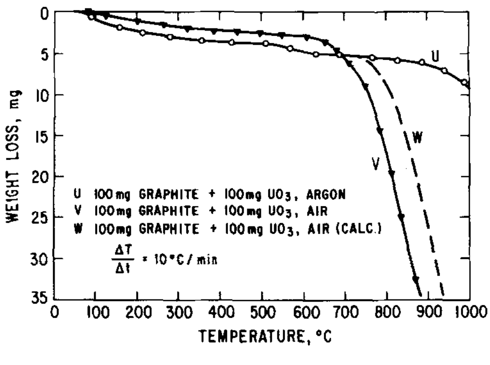

FIG. 5. Weight loss vs temperature thermograms for a mixture of 100 mg graphite + 100 mg UO_3 in flowing argon (U) and air (V). Curve W shows calculated weight losses for a similar graphite–UO_3 mixture in the absence of catalysis.

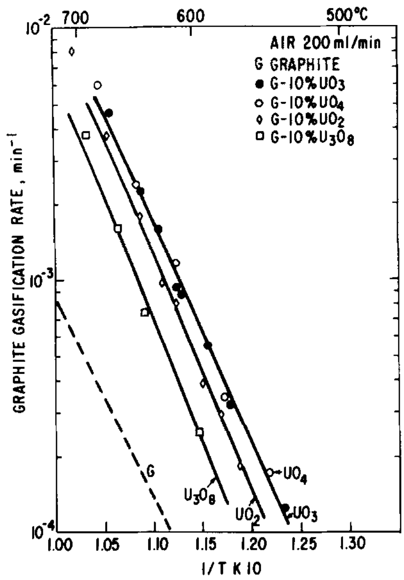

FIG. 6. Arrhenius plots (log gasification rate vs 1/*T*) for pure graphite and graphite doped with 10 wt% UO_2, U_3O_8, UO_3, and UO_4.

uranyl nitrate and acetate decompose to this oxide on heating and because of the low decomposition temperatures (300–400°C), the resulting UO_3 product is likely to be finely dispersed over the graphite substrate. The high degree of subdivision of the oxide phase probably accounts for the strong catalytic effect exhibited by these uranyl salts.

The phase relations in the U–O system are very complex (*15*). In addition to the well-characterized oxides UO_2, U_3O_8, and UO_3 a large number of intermediate oxides and nonstoichiometric phases have been identified. The oxides readily interconvert at elevated temperatures and there is often a continuous transition from one lattice structure to another. For example, the cubic face-centered oxide UO_2 (which has a composition range from $UO_{1.75}$ to $UO_{2.3}$) readily takes up oxygen on heating forming $UO_{2.5}$ (orthorhombic), $UO_{2.67}$ or U_3O_8 (orthorhombic), and $UO_{3.0}$ (hexagonal). UO_3, and to some extent U_3O_8, lose oxygen on heating to higher temperatures to form UO_2 and intermediate phases. U_3O_8 and UO_3 are also reduced to UO_2 on heating with carbon.

Assuming that the species UO_3 is the active catalytic entity in the uranium-catalyzed oxidation of carbon, a likely redox cycle which would account for the catalysis is the sequential occurrence of the reactions

$$UO_3 + C = UO_2 + CO \qquad (1)$$

$$UO_2 + \tfrac{1}{2}O_2 = UO_3 \qquad (2)$$

That this reaction sequence is possible under the conditions of catalyzed gasification is shown by the strongly negative free energies of these reactions in the temperature range 500–1000°C. Alternatively, a nonstoichiometric lower oxide may be formed as an intermediate. The rate-determining step of the catalyzed process is not known at this point, however, the kinetics of the overall reaction will depend on the degree of dispersion of the oxide catalyst particles on the graphite surface.

SEM examination of natural graphite flakes on which had been evaporated dilute solutions of uranyl acetate followed by oxidation in air at 900°C, revealed large numbers of hexagonal pits on the graphite basal plane surface. Catalyst particles were often found to be adhering to the sides of these pits, which presented a serrated appearance. Catalyst particles were also observed to congregate at the edges of the graphite flakes where gasification was most marked, resulting in a scalloped morphology. Because of the very high melting point of uranium oxide (>2800°C), the particles do not exhibit the liquid-like mobility on the graphite surface frequently observed with other catalysts (*8*).

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