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Studies of Topochemical Heterogeneous Catalysis

IV. Catalysis of the Reaction of Zinc Sulphide with Oxygen

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The reaction of zinc sulphide with oxygen to form zinc sulphate may be promoted by the addition of a supported platinum catalyst, but the reaction yield is limited by the blocking of the substrate surface by the reaction product. The reaction is a further example of topochemical heterogeneous catalysis involving diffusion of activated oxygen from the catalyst to the substrate surface. The reaction of platinum-coated zinc sulphide with oxygen is almost instantaneous at temperatures as low as 550°C to form ZnO, while in the absence of catalyst slow formation of ZnO occurs only above 620°C. The "catalysis" observed for platinum-coated zinc sulphide is a result of the temperature increase due to catalysis of the reaction of SO_2 with oxygen. This reaction and the temperature increase may be arrested by diluting the sample with silica, when the product of reaction with oxygen is again zinc sulphate.

INTRODUCTION

Previous work has shown that the reaction of gaseous oxygen with UF_4 (*1,2*), and the reactions of Fe_2O_3, UO_3, V_2O_5, and UO_2F_2 with hydrogen gas (*3*) may be catalyzed by platinum either supported on the above substrates or on an inert support which is mixed with the substrate. These reactions are examples of topochemical heterogeneous catalysis and involve the formation on the catalyst of activated oxygen or hydrogen species which are transferred both by surface and gas diffusion to react at the substrate surface. The UF_4-O_2 reaction appeared to be a unique example of a catalyzed reaction between a solid substrate and oxygen gas and other examples were sought with which this reaction could be compared. The reaction of zinc sulphide with oxygen gas was chosen as a likely possibility. The path of this reaction is temperature dependent (*4,5*), the product in the absence of catalyst being zinc sulphate at low temperatures [Eq. (1)], while above 600°C zinc oxide is formed either by direct reaction of zinc sulphide [Eq. (3)] or at higher temperatures through decomposition of zinc sulphate [Eq. (2)].

$$ZnS + 2O_2 \longrightarrow ZnSO_4, \qquad (1)$$

$$ZnSO_4 \longrightarrow ZnO + SO_3, \qquad (2)$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2. \qquad (3)$$

Lemmerling and Van Tiggelen (*4*) studied the formation of zinc sulphate in the absence of interfering reactions between 160 and 250°C, by measuring pressure changes due to oxygen uptake by zinc sulphide. Despite the slow reaction rate, they were able to calculate activation energies of 24 and 19 kcal $mole^{-1}$ respectively for the two steps they proposed in the formation of zinc sulphate:

$$ZnS + O_2 \longrightarrow ZnS\,(O_2)_{ads}, \qquad (4)$$

$$ZnS\,(O_2)_{ads} \longrightarrow ZnSO_4. \qquad (5)$$

The addition of greater than 20% by

weight of copper oxide has been shown to promote the formation of zinc sulphate (*6*) by catalyzing the reaction with oxygen of SO_2 formed by reaction (3):

$$2SO_2 + O_2 \longrightarrow 2SO_3, \qquad (6)$$

$$SO_3 + ZnO \longrightarrow ZnSO_4. \qquad (7)$$

This paper examines the catalysis by platinum of the direct addition of oxygen to zinc sulphide to form zinc sulphate.

EXPERIMENTAL

Zinc sulphide powder obtained from Merck was sieved and the −300 mesh fraction used for all studies. This material was coated with platinum by slurrying with the appropriate weight of dichlorobis(triphenylphosphine) platinum (II)[1] dissolved in dichloromethane and evaporating to dryness in a rotary evaporator. The sample was heated for 3 hr in flowing hydrogen at 400°C to reduce the platinum complex to platinum metal.

1% platinum on alumina catalyst −180 + 240 mesh was supplied by Engelhard Industries Ltd.

The oxygen and nitrogen used were "medical dry" and "high purity dry" grades obtained from Commonwealth Industrial Gases Ltd (Australia). Gases were dried by passage through two columns filled with molecular sieves.

Reaction rates were measured using a Cahn thermobalance (Type RG 2000) and flowtube reactor as described previously (*1*). Weight losses were recorded on a Rikadenki (Model B261) recorder. Gas flow rates of 900 cm^3 min^{-1} and sample weights of 50 mg were used.

RESULTS

TABLE 1
Rapid Reaction of Platinum Coated ZnS with Oxygen

Pt wt% on ZnS[a]	0.1	0.5	1.0	5.0	2.0
Initiation temperature (°C)	710	630	580	560	505[b]

[a] 50 mg sample spread uniformly on pan.
[b] 50 mg sample heaped on pan.

A maximum catalytic effect is to be expected when the catalyst is deposited directly on the surface of the reacting substrate. Samples of zinc sulphide were coated with varying concentrations of platinum and exposed to oxygen at constant temperatures between 500 and 700°C. For each sample, a temperature was found below which there was no measurable reaction (Table 1), but above which almost instantaneous reaction of zinc sulphide occurred to produce zinc oxide (Fig. 1). The reaction was highly exothermic, and although the increase in temperature registered by a thermocouple located several millimeters above the sample pan was over 60°, the actual increase in the temperature of the sample would have been considerably greater. It was also noted that the initiation temperature was lowered and the observed temperature excursion increased if the sample was heaped rather than being spread uniformly over the sample pan. In each case a stoichiometric yield of ZnO was obtained and SO_3 was confirmed as a reaction product by the white fumes observed when the exit gas was exposed to

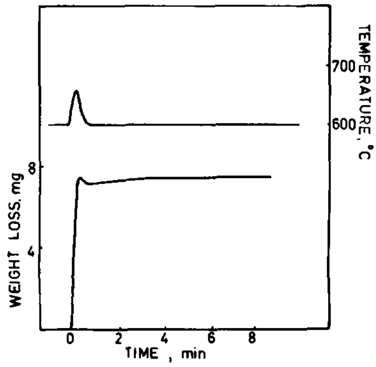

Fig. 1. Formation of ZnO by reaction in oxygen at 600°C of ZnS (50 mg) coated with 1 wt% Pt.

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[1] Prepared from choloroplatinic acid [Ref. (*7*)].

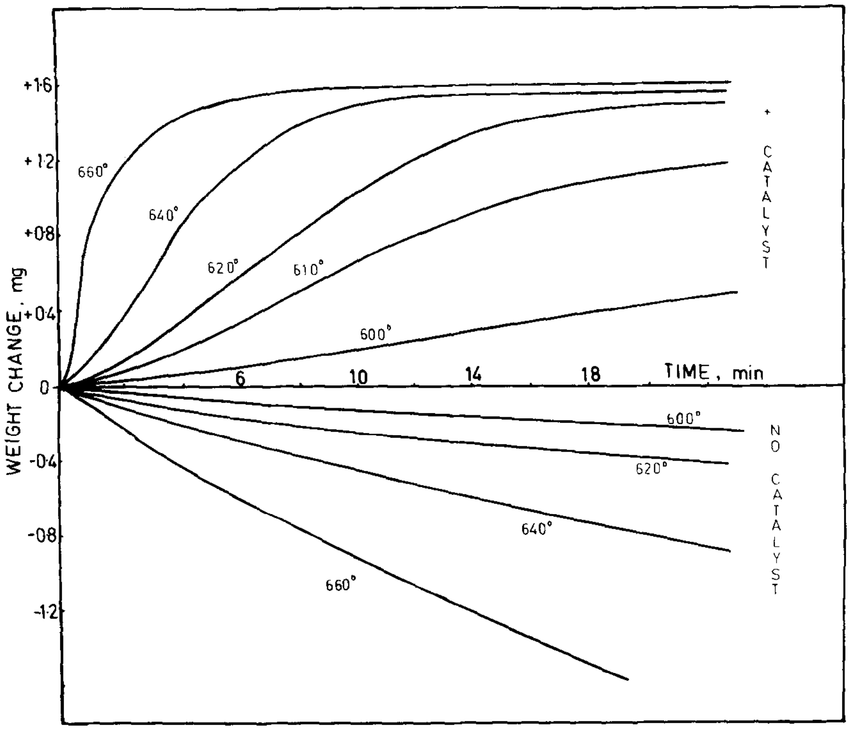

FIG. 2. Effect of temperature on the reaction of ZnS (50 mg) with oxygen (a) in the presence of 5 wt% of 5% Pt on alumina catalyst (−180 + 240 mesh) to form $ZnSO_4$; (b) in the absence of catalyst to form ZnO.

moist air. In the absence of catalyst, the reaction of ZnS proceeds only slowly to ZnO at temperatures greater than 620°C (Fig. 2).

Believing that the temperature excursion was the result of the exothermic, catalyzed reaction of SO_2 with oxygen, attempts were made to mitigate the effect of this reaction by mixing an inert diluent such as silica with the sample. Under these conditions, a weight gain due to zinc sulphate formation was observed, without a measurable temperature increase (Table 2). The reaction was rapid, with the observed weight gain increasing with increasing temperature. At 670°C there is an ensuing weight loss probably due both to the decomposition of $ZnSO_4$ and to the direct conversion of ZnS to ZnO.

When a mixture of zinc sulphide and an alumina-supported platinum catalyst was reacted with oxygen, a weight gain was again observed, the magnitude of which increased with increasing catalyst concentration (Table 3). The maximum weight gain observed corresponded to only a 7% conversion to zinc sulphate.

For catalyst concentrations below 5 wt% the weight gain reaction involved an initial fast reaction followed by a second slower reaction. For 5 wt% catalyst and above, a single first order reaction step was observed (Fig. 3). Similar behavior was observed previously for the reaction

TABLE 2

REACTION WITH O_2 OF PLATINUM COATED ZnS DILUTED WITH SILICA[a]

Temperature (°C)	Maximum weight gain (mg)	$ZnSO_4$ yield (%)
500	0	0
550	0.15	4.8
610	0.25	8.0
670	0.22	7.0

[a] 5 mg 5 wt% Pt on ZnS + 45 mg SiO_2.

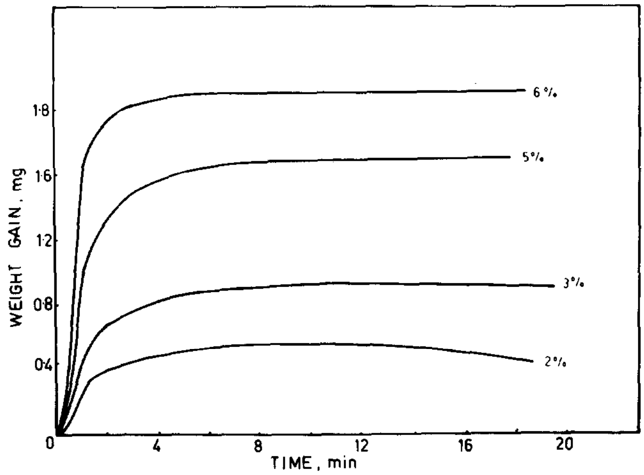

FIG. 3. Effect on the reaction of ZnS (50 mg) with oxygen of varying percentages by weight of 5% Pt on alumina catalyst at 663°C.

of UO_3 with hydrogen in the presence of a platinum catalyst (*8*).

With a catalyst concentration of 6 wt%, the weight gain due to zinc sulphate formation was accompanied by a measurable temperature increase of several degrees, however for 10 wt% catalyst this increase was much greater and the partial weight gain was interrupted by a rapid weight loss as observed previously for samples of platinum-coated zinc sulphate.

An analysis of a 50 mg sample of ZnS containing 8 wt% platinum on alumina catalyst, after 12 minutes reaction with oxygen at 650°C showed the product to contain 11.0 wt% zinc sulphate, equivalent to a conversion of 7.5% of the ZnS. The weight gain measured from the thermogram corresponded to the formation of 7.3 wt% zinc sulphate. X-Ray diffraction studies indicated that the product consisted of a mixture of ZnS and $ZnSO_4$ with no detectable ZnO. By comparison, it was found that in the absence of catalyst at 650°C after the same reaction time, 4.3% of the zinc sulphide was converted to ZnO.

TABLE 3
EFFECT OF CATALYST CONCENTRATION ON THE $ZnS-O_2$ REACTION[a]

Catalyst wt% with ZnS	1	2	3	4	5	6	9	10
Yield of $ZnSO_4$ (%)	0	1.6	2.9	4.5	5.3	6.2	7.7	1.8[b]

[a] 5 wt% Pt on Al_2O_3 (−180 + 240 mesh) 663°C.
[b] Followed by rapid weight loss.

DISCUSSION

It is well-known that platinum will catalyze the reaction of SO_2 with oxygen to produce SO_3. At temperatures where zinc sulphate is known to react with oxygen to produce zinc oxide, it is likely that some of this SO_2 will react with oxygen in the presence of platinum before it can diffuse from the substrate into the flowing gas stream. Since this reaction is highly exothermic, it will bring about a considerable localized increase in the temperature of the sample which by an autocatalytic process will further promote the oxidation of zinc sulphide to zinc oxide. The temperature at which this reaction initiation will occur will be dependent on catalyst concentration. By heaping the sample, less SO_2 can be expected to diffuse from the substrate without reacting with the catalyst, and at the same time the reaction heat will be stored more effectively. These reaction conditions differ from those of Germain-Lefevre *et al.* (*6*) who proposed that, in static air, recombination of SO_3 with ZnO can occur to give $ZnSO_4$. Such a reaction would be unlikely to occur to a measurable extent in a flowing gas stream. By diluting the sample with silica, the temperature-induced "catalysis" is prevented, and instead the direct catalysis of zinc sulphate formation can be observed. A similar situation is achieved if a separated platinum catalyst is used.

The main difference between the catalysis of this reaction and that of the UF_4–oxygen reaction is that the product of the $ZnS–O_2$ reaction coats unreacted zinc sulphide, inhibiting further reaction, whereas the vaporization of UF_6 from the surface of UF_4 presumably creates channels permitting further propogation of the reaction. The first step in the $ZnS–O_2$ reaction is the diffusion of activated oxygen from the catalyst to neighboring zinc sulphide particles where reaction occurs. If it is also assumed that surface diffusion of activated oxygen over zinc sulphate cannot readily occur, it is possible to understand why the yield of zinc sulphate should be low and should be increased by increasing the catalyst concentration. Further, it is possible to envisage a situation where two processes are contributing to the overall reaction; a rapid surface diffusion to zinc sulphide in close proximity to the catalyst and a slower reaction controlled by gas diffusion to further removed zinc sulphide particles. Increasing the catalyst concentration will increase the contribution of the first reaction until a concentration is reached at which all reaction occurs by this mechanism. Increasing the temperature, for any catalyst concentration will increase the flux of activated oxygen leaving the catalyst surface, so that the distance traveled before the reaction ceases will also increase. This reaction will occur more efficiently with catalyst deposited on ZnS provided that dilution with silica has removed the temperature increase due to the $SO_2–O_2$ reaction, and the rapid weight gain observed at all temperatures studied demonstrated this increased efficiency. In fact the reaction could not be slowed down by decreasing the temperature; this only decreased the yield of $ZnSO_4$ produced.

While the catalyzed formation of zinc sulphate results in a weight gain, the reaction at the same temperatures in the absence of catalyst involves a weight loss with zinc oxide formation. It is important to know the contribution of the weight loss reaction to the observed weight gain. With increasing concentrations of separated catalyst, the increased rate of the catalyzed reaction diminishes the contribution of the uncatalyzed reaction. At 660°C, using 2 wt% of separated catalyst the observed weight gain corresponds to a 1.6% conversion of ZnS to $ZnSO_4$. The thermogram shows a gradual weight loss following the initial gain and X-ray analysis confirmed the presence of ZnO in the product. This ZnO is not formed from the decomposition of zinc sulphate since at the same temperature using a higher catalyst concentration, the thermogram registers a constant weight for some 20 min following the initial weight gain, while no ZnO is found in the reaction product. Under these latter conditions blockage of surface sites by zinc sulphate is no doubt responsible for the prevention of ZnO formation.

Similarly as the temperature is increased for a particular catalyst concentration, the blocking of surface sites will affect the contribution of the uncatalyzed reaction. Attempts to measure the activation energy for the catalyzed reaction revealed the complexity of the diffusion kinetics. Whereas in the catalyzed oxidation of UF_4 the rate-controlling process involves the formation of activated oxygen species, for the catalyzed ZnS oxidation this process is compounded by the inhibition of the oxygen diffusion process by surface blockage. Data obtained for 5 wt% of separated catalyst clearly reveal the temperature dependence of the reaction kinetics (Fig. 2). At low temperatures the curves are sigmoidal changing to linear at higher temperatures. This type of behavior is analogous to that of self-catalyzed nucleation observed in some solid state reactions (*9,10*).

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