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Studies of Topochemical Heterogeneous Catalysis

I. The Catalytic Effect of Platinum on the Reaction of UF_4 with O_2, and of UO_2F_2 and UO_3 with H_2

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The rate of the oxidation of UF_4 according to the equation $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$, the rate of reduction of UO_2F_2 according to the equation $UO_2F_2 + H_2 \rightarrow UO_2 + 2HF$, and the rate of reduction of UO_3 to UO_2 were observed to be enhanced by the addition to the substrate of small quantities of platinum in the form of metallic platinum supported on γ-alumina. The phenomenon was studied in detail and it was observed that the apparent activation energies of the catalyzed and uncatalyzed rates were the same, the effect of the catalyst being to increase the preexponential factor of the Arrhenius equation. The results suggest that the gaseous reactant, either O_2 or H_2, is adsorbed onto the catalyst surface and dissociated into atoms or some other activated species which subsequently desorb, migrate away from the catalyst surface and react with the substrate. Results are presented which suggest that in the case of oxygen the migration of the active species from the catalyst to the substrate occurs at least in part by the diffusion of the active species through the gas phase.

INTRODUCTION

In recent years several authors have described results which showed that the rates of reduction of a variety of metal oxides by hydrogen can be greatly enhanced by the addition of traces of certain metal catalysts, notably platinum (*1*). An unusual aspect of this effect is that in some cases the catalyst, either in the form of a finely divided metal or as the metal supported on an inert carrier material, was simply mixed with the oxide to be reduced. This phenomenon has been termed topochemical heterogeneous catalysis by a recent reviewer (*2*), who also emphasized the limited extent of understanding of the mechanism of this effect and the absence of detailed experimental results which might make such understanding possible.

The Fluorox reactions [Eqs. (1–3)] are a series of three reactions

$$2UF_4 + O_2 \xrightarrow{800°C} UO_2F_2 + UF_6, \tag{1}$$

$$UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF, \tag{2}$$

$$UO_2 + 4HF \longrightarrow UF_4 + 2H_2O, \tag{3}$$

consisting of the oxidation of UF_4 by O_2 at temperatures near 800°C to yield UO_2F_2 and UF_6, followed by reduction of UO_2F_2 to UF_4. The oxidation reaction [Eq. (1)] is unusual and has been the subject of several previous studies (*3*), but the main interest in the above reactions is technological since they potentially form the basis of a commercial process for the production of UF_6 by a method not requiring the use of fluorine. However, attempts to develop this process have shown that the high temperatures (>800°C) required to give economical rates of reactions for the oxidation reaction give rise to excessive corrosion and to sintering of the UF_4 (*4*).

Preliminary work (*5*) in this laboratory

TABLE 1

ORIGIN AND PROPERTIES OF MATERIALS USED IN THIS WORK

Material	Origin	Av particle size[a] (μm)	Surface area (m^2 g^{-1})[b]
UF_4	ex ADU	150–250	1.9
UF_4	Merck	~30	2.3
UF_4	RIC[c]	~1[d]	0.3
UO_2F_2	ex ADU	150–250	8.3
UO_3	Denitrator	75–125	1.4
UO_3	ex ADU	75–125	14.0

[a] Average particle size determined by sieving the material.

[b] Measured by BET method.

[c] Research Inorganic Chemicals Inc.

[d] Estimated from microscope measurements.

had shown that the rate of reaction (1) could be greatly enhanced by the presence of traces of platinum physically mixed with the UF_4 particles. These results were of sufficient interest to warrant a more detailed study of the phenomenon; the results obtained are described in this paper.

METHODS

Materials. Two types of UO_3 were used in this work, one being prepared by thermal denitration of an aqueous solution of uranyl nitrate in a spray dryer (*6*), the other by precipitating ammonium diuranate (ADU) at pH 7.5 by adding NH_4OH to a continuously stirred solution of uranyl nitrate maintained at 50°C. The ADU precipitate was washed, dried, and converted to UO_3 by heating in a stream of air at 350°C. UF_4 from two commercial sources (Merck and Research Inorganic Chemicals Inc.) was used in this work. A further sample was prepared by hydrogen reduction and subsequent hydrofluorination at 500°C of UO_3 prepared by the ADU method described above. UO_2F_2 was prepared by reacting UO_3 (ADU derived) with a gaseous HF/O_2 mixture at 500°C. After preparation all of the above compounds were ground and sieved into the required size fractions, and the surface area and particle size were measured (Table 1).

A variety of catalysts was used in this work. Their origin and, where applicable, their method of preparation, are summarized in Table 2. The catalyst/substrate mixtures were prepared by weighing out the appropriate amounts of materials and mixing by mechanical shaking. In this work the catalyst concentration is expressed as weight percent, i.e., 100 [wt of catalyst/wt

TABLE 2

ORIGIN AND PROPERTIES OF CATALYSTS USED IN THIS STUDY

Catalyst	Catalyst no.	Origin or method of preparation[a]	Particle size (μm)
5 wt% Pt on γ-Al_2O_3	1	a	Very fine powder, 50% less than 5 μm diam
5 wt% Pt on γ-Al_2O_3	2	a	150–75
5 wt% Ru on γ-Al_2O_3	3	b	<50
5 wt% Ir on γ-Al_2O_3	4	b	<50
5 wt% Os on γ-Al_2O_3	5	b	<50
5 wt% Pd on γ-Al_2O_3	6	b	<50
5 wt% Rh on γ-Al_2O_3	7	b	<50
5 wt% Au on γ-Al_2O_3	8	b	<50
5 wt% Ag on γ-Al_2O_3	9	b	<50
PdO_2 (unsupported)	10	a	<50
5 wt% NiO γ-Al_3O_3	11	c	<50

[a] (a) Catalysts obtained from Engelhard Industries. (b) These catalysts were prepared by slurrying an aqueous solution of metal salt with an appropriate quantity of support, evaporating to dryness in a rotary evaporator, drying in air at 100°C for 2 hr and then heating in hydrogen at 300°C for 2 hr. (c) As for (b) but heated in air at 600°C for 4 hr.

of substrate]. Platinum was deposited onto UF_4 and UO_3 by slurrying them with an aqueous solution containing chloroplatinic acid, followed by drying in a rotary evaporator, further drying at 110°C and finally heating at 400°C in a stream of hydrogen, or in the case of the UO_3, in nitrogen. Catalyst pellets, consisting of 0.1 wt% Pt on γ-alumina cylinders (3 mm diam × 6 mm) were obtained from Engelhard Industries.

The oxygen and nitrogen used in this work were, respectively, of "Medical Dry" and "High Purity Dry" grades obtained from Commonwealth Industrial Gases Limited (Australia). The hydrogen was of a commercial purity and was obtained from the same source. All gases were dried by passage through two columns (1 m long, 5 cm diam) filled with activated molecular sieves. The reaction of UF_4 with O_2 is particularly sensitive to the presence of traces of water, and great care had to be taken that all the equipment and reagents used in the study of this reaction were free from residual moisture.

Measurement of Reaction Rates. The reaction rates were measured using a thermobalance (Cahn, Type RG 2000) in conjunction with a conventional flowtube reactor. The temperature of the sample was measured with a Pt/Rh thermocouple positioned approximately 5 mm above the center of the sample pan. For the UF_4 reactions, 30 mg samples were used, while 100 mg samples of UO_2F_2 and UO_3 were required to give acceptable weight changes in the course of the reduction of these compounds. This size of sample formed a layer less than 1 mm thick on the nickel or gold pan of the sample holder. Typical gas flowrates were 900 cm^3 min^{-1} and preliminary experiments showed that the reaction rates were independent of gas flowrates in the range 200–2000 cm^3 min^{-1}, and independent of sample size in the range 10–300 mg.

Results

The Reaction of UF_4 with O_2. Typical reaction curves obtained at 640°C and using ADU derived UF_4 with catalyst No. 1 are illustrated in Fig. 1. The catalytic effect of platinum is readily observable in samples containing only 0.1 wt% of catalyst, but it may be noted that in this case no further increase in the reaction rate is observed when the catalyst concentration is increased from 1 to 5 wt%. If, however, these experiments were repeated with the larger particle size catalyst (catalyst No. 2) it was found that the rate of reaction

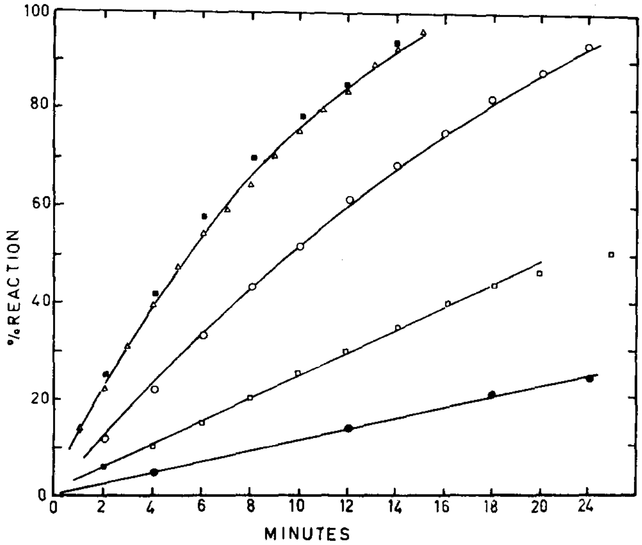

FIG. 1. Effect of catalyst concentration (catalyst No. 1) on the rate of oxidation of the ADU derived UF_4 at 640°C. (●) No catalyst, (□) 0.1 wt%, (○) 0.5 wt%, (△) 1 wt%, (■) 5 wt%.

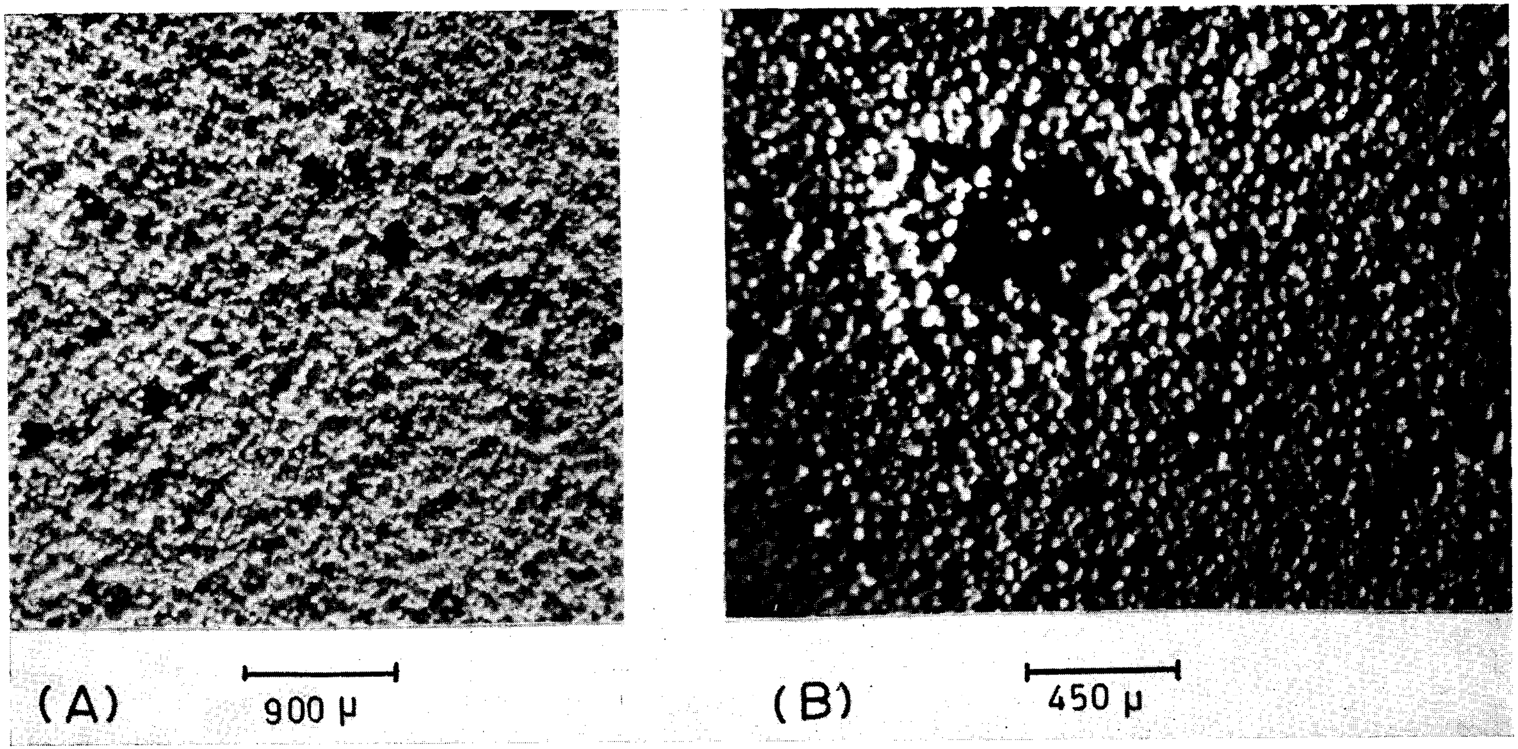

FIG. 2A. Typical appearance of a sample of Merck UF_4 containing 1 wt% of catalyst No. 2. (B) Detail of the appearance of the UF_4 in the immediate vicinity of a catalyst particle after a 3 min exposure to O_2 at 640°C. The conversion of the dark green UF_4 to light yellow UO_2F_2 around the catalyst particle can be clearly seen.

was slower compared to that obtained with the fine catalyst, but continued to increase up to 10 wt% catalyst. This observation is probably a reflection of the importance of catalyst–UF_4 contact in the present system, which will be maximized by the use of a small particle size catalyst.

The catalytic effect of platinum is particularly unusual when the nonhomogeneous distribution of catalyst particles in the UF_4 is considered (Fig. 2A). As expected, in the initial stages of the reaction only the UF_4 in the immediate vicinity of a catalyst particle was converted to UO_2F_2 (Fig. 2B), but it was observed that if the sample was exposed to O_2 for longer periods, the zones of reacted UF_4 around each catalyst particle gradually extended until they coalesced. These observations suggest that the active species formed on the catalyst surface are capable of leaving the catalyst surface and migrating for quite large distances before reacting with the UF_4.

An even more noticeable catalytic effect was observed when the platinum was deposited directly on the UF_4 rather than being placed on an inert carrier which was subsequently mixed with the substrate (Fig. 3). Under these circumstances, the catalyzed rate was quite rapid at temperatures as low as 500°C where the uncatalyzed rate was so slow as to be virtually imperceptible. It was also noted that a sample of UF_4 not containing any added catalyst reacted significantly faster when suspended on a platinum pan compared to a similar sample placed on a gold pan. For example, at 600°C, a sample of UF_4 placed on a platinum dish underwent 30% reaction in 32 min, while a sample placed on a gold dish underwent 15% reaction in the same time.

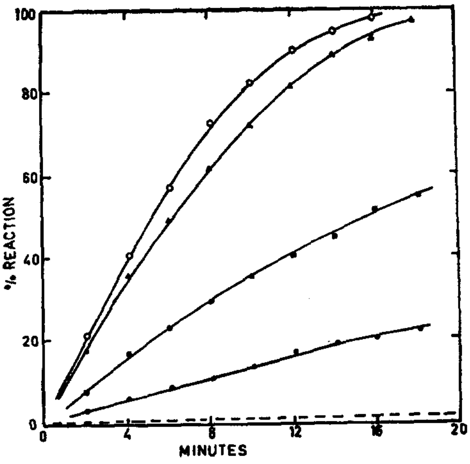

Fig. 3. Effect of platinum concentration on the rate of oxidation of Merck UF_4 at 500°C. For these runs the platinum was deposited directly onto the UF_4 surface. (– –) Uncatalyzed reaction, (●) 0.001 wt% Pt, (■) 0.01 wt% Pt, (▲) 1.0 wt% Pt, (○) 2.0 wt% Pt.

In a series of experiments at 640°C using 4–6 g of UF_4 containing 1 wt% of catalyst No. 1 the yields of UO_2F_2 at the completion of the reaction were in the range 93–99% of the theoretical yield according to the stoichiometry of Eq. (1). The yields of UF_6 (identified by ir spectroscopy) were in the range 40–50% theoretical, but these low yields are probably a reflection on the well-known difficulty of quantitatively collecting small amounts of UF_6 rather than the result of some complication in the stoichiometry of the reaction. It was also noticed that the weight losses observed in the thermobalance experiments on the oxidation of UF_4 were invariably within 2–4% of the theoretical weight loss calculated according to Eq. (1).

A large number of metals other than platinum were tested as potential catalysts for the UF_4–O_2 reaction. As illustrated in Fig. 4, platinum was found to be the best catalyst, but several other group VIII metals, notably ruthenium, palladium and iridium were also found to catalyze the UF_4–O_2 reaction. It may be noted that the determination of true catalytic activity of a series of catalysts is a problem of considerable experimental difficulty, since factors such as the dispersion and crystallite size of the catalytic metal, and the particle size distribution of the support material would have to be identical for all the catalysts to be compared.

The effect of reaction temperature on the rate of reaction (measured as the initial rate) of UF_4 with O_2 both in the presence and absence of catalysts is summarized in Fig. 5; the data are plotted according to the usual Arrhenius equation. The results

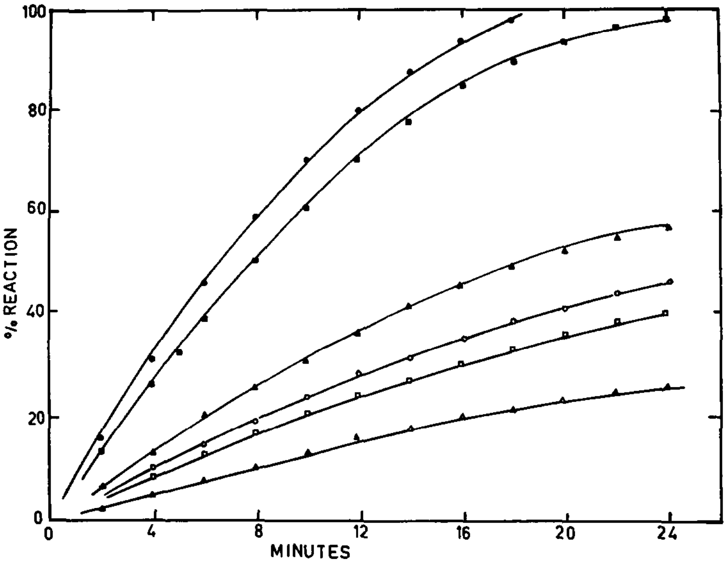

FIG. 4. Effect of various catalysts on the rate of oxidation of ADU derived UF_4 at 640°C. All catalyst concentrations are 1 wt%: (●) Pt, catalyst No. 1; (■) Ru, catalyst No. 3; (▲) Ir, catalyst No. 4; (○) Os, catalyst No. 5; (□) Pd, catalyst No. 6; (△) no catalyst.

show that, within the experimental error, the activation energies of the reaction both in the presence and absence of the catalysts are the same at 24 ± 2 kcal $mole^{-1}$, the enhancement of the reaction rate in the presence of the catalysts being reflected in an increase in the preexponential factor. A similar effect is noted when comparing the Arrhenius plots of the two different types of UF_4 used in this work (RIC, surface area 0.3 m^2 g^{-1}, and Merck, surface area 2.3 m^2 g^{-1}). As might be expected, the low surface area material reacted somewhat slower than the high surface area material, but again, a smaller preexponential factor rather than in a change in the activation energy was observed.

As discussed below, the present results suggest that an active species, which is formed on the catalyst surface, can migrate

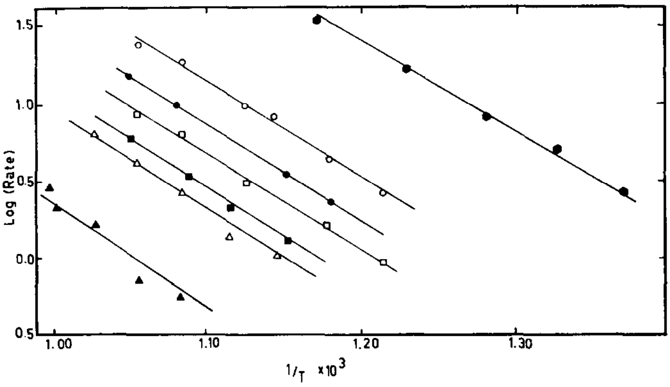

FIG. 5. Arrhenius plots of various catalyzed and uncatalyzed oxidations of UF_4. (▲) RIC UF_4, no catalyst; (■) RIC UF_4 with 1 wt% of catalyst No. 3; (●) RIC UF_4 with 1 wt% of catalyst No. 1; (△) Merck UF_4, no catalyst; (□) Merck UF_4 with 1 wt% catalyst No. 3; (○) Merck UF_4 with 1 wt% catalyst No. 1; (M) Merck UF_4, 1 wt% Pt on UF_4 surface.

for considerable distances before reacting with the UF_4 substrate. This migration can conceivably occur by surface diffusion via catalyst and UF_4 particles which are in contact, or by diffusion of the active species through the gas phase. In an attempt to estimate the importance of the latter possibility, a device (Fig. 6a) was constructed which enabled the accurate positioning of a catalyst pellet small distances above the surface of a lightly pressed UF_4 pellet. The device containing a UF_4 pellet was suspended in the furnace tube and exposed to O_2 gas at 640°C for various periods. As shown in Fig. 6b the appearance of the UF_4 pellet after this treatment shows that the UF_4 immediately below the surface of the catalyst pellet has reacted to a much greater extent than the UF_4 further away. This observation suggests that at least some of the active species do leave the catalyst surface and diffuse to the UF_4 through the gaseous phase. In a similar experiment, the UF_4 pellet was replaced by a gold disk and the device was exposed to O_2 gas at 640°C for 24 hr, after which the gold disk was removed from the apparatus and examined with a microscope. No indication of any platinum transferred from the catalyst surface to the disk was found.

The Reaction of UO_2F_2 and UO_3 with H_2. Following the observation of the unusual catalytic effect of platinum on the UF_4–O_2 reaction, preliminary experiments showed that the rate of reduction of UO_2F_2 by H_2 was similarly affected by the presence of platinum. These observations were confirmed by measurements of the rate curves for samples containing various concentrations of catalysts (Fig. 7). As was found with the UF_4–O_2 reaction, these results also showed that the catalytic effect of platinum is readily noticeable at catalyst concentrations as low as 0.1 wt% and that no further enhancement in the rate is observed if the catalyst concentration exceeds 1 wt%. Measurements of the activation energies in the temperature range 600–750°C of the catalyzed (1 wt% catalyst No. 1) and uncatalyzed reactions indicated that these were again the same within our experimental error (27 ± 2 kcal mole^{-1}), but in contrast to the UF_4–O_2 reaction, the reduction of UO_2F_2 by H_2 was found to be catalyzed by a wide range of catalytic materials (Table 3) including such metals as silver and nickel.

The reduction of UO_3, prepared by the denitrator route was also found to be catalyzed by the addition of the platinum catalyst as well as a series of other metals (Table 3). By analogy with our observations of the UF_4–O_2 reaction, the deposition of platinum directly onto the UO_3 surface resulted in a very marked catalytic effect. For example, a sample of denitrator UO_3 coated with 1.0 wt% of platinum was completely reduced in 4 min at 300°C, while in the absence of catalyst the reduction of a similar sample was only 5% complete.

The activation energies of the uncatalyzed and catalyzed (by 1 wt% of catalyst No. 1) reactions were determined in the temperature range 450–600°C and found to be 29 and 30 kcal mole^{-1}, respectively.

In contrast to the denitrator UO_3, the ADU derived material is reduced rapidly at temperatures as low as 400°C, this observation probably being a reflection of the much larger surface area of the ADU-

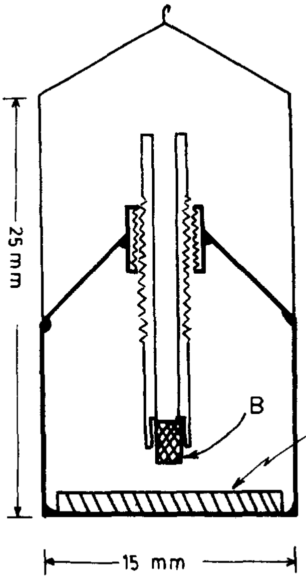

FIG. 6a. Apparatus used to position catalyst pellet small distances above UF_4 surface. (A) UF_4 disk, (B) catalyst pellet.

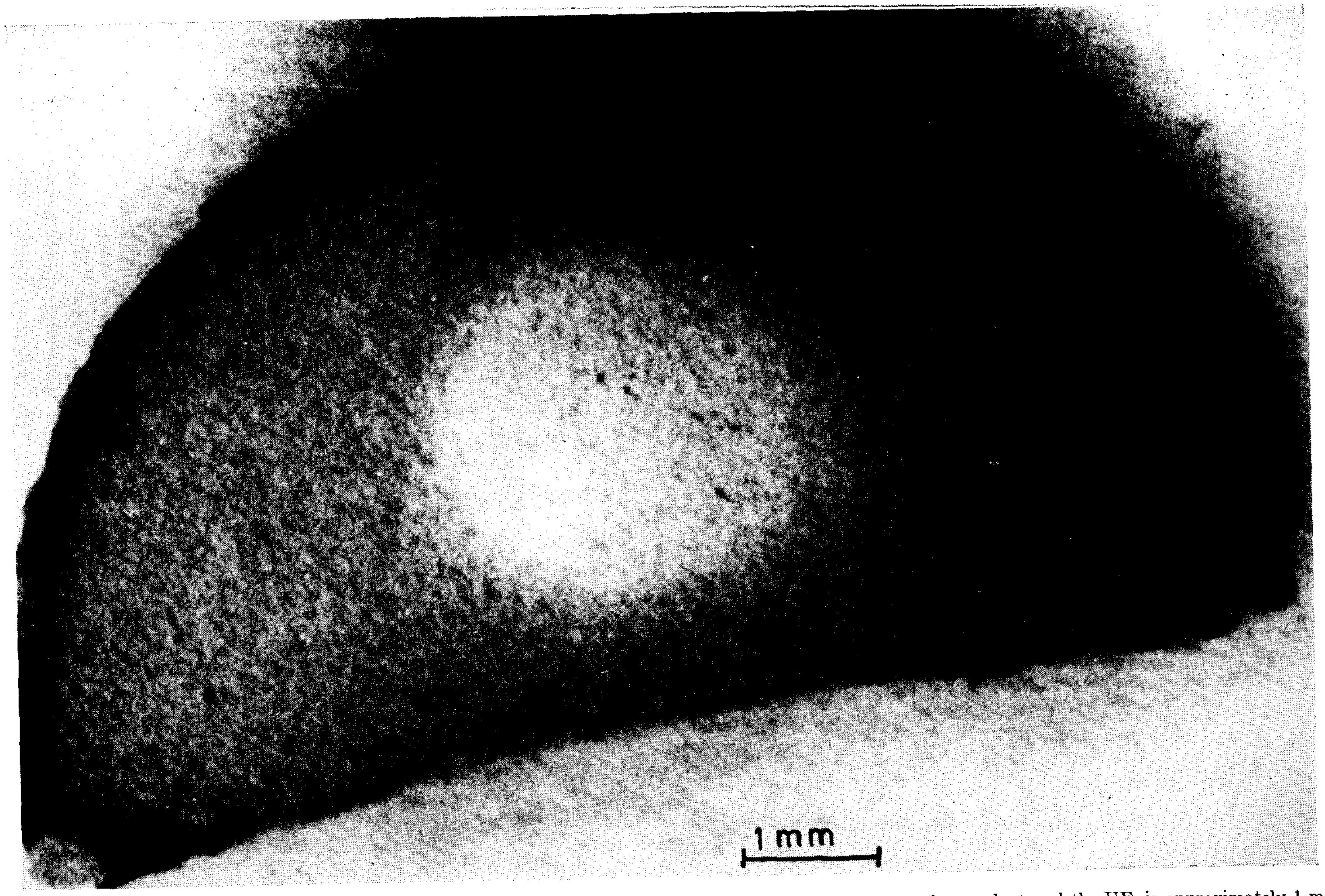

Fig. 6b. Typical appearance of UF_4 pellet after 10 min exposure to O_2 at 640°C; the distance between the catalyst and the UF_4 is approximately 1 mm. The conversion of the UF_4 to UO_2F_2 in the area immediately below the catalyst is indicated by the light colored area in the center of the UF_4 disk.

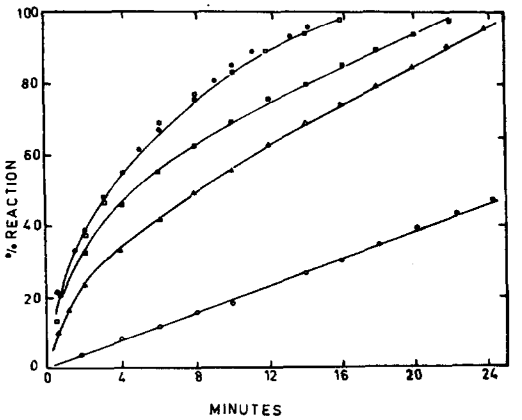

FIG. 7. Effect of catalyst concentration on the reduction of UO_2F_2 at 600°C. The concentrations of catalyst No. 1 were: (○) 0 wt%; (△) 0.1 wt%; (■) 0.5 wt%; (●) 1 wt%; (□) 2.5 wt%.

UO_3. Further, the addition of the supported platinum catalyst (catalyst No. 1) to the ADU–UO_3 was found to have only a marginal effect on the rate of reduction (Fig. 8), but the deposition of the platinum directly onto the surface of the particles was observed to increase the rate dramatically, a sample containing 5 wt% platinum being reduced very rapidly at temperatures as low as 100°C. These observations again indicate the importance of catalyst–substrate contact in the catalysis of reactions occurring at the lower temperatures.

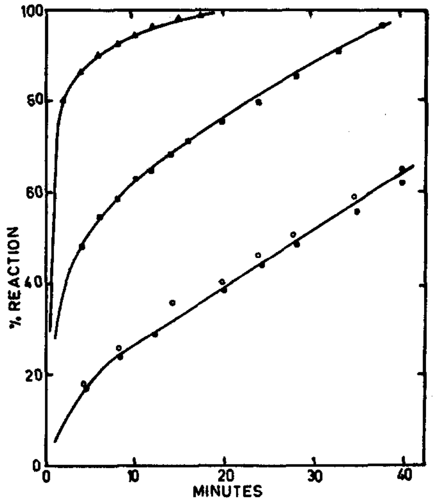

FIG. 8. Effect of platinum on the reduction of the ADU derived UO_3 at 350°C. (●) No catalyst, (○) 1 wt% catalyst No. 1, (■) 0.01 wt% Pt deposited on UO_3, (▲) 0.1 wt% Pt deposited on UO_3.

TABLE 3

COMPARISON OF THE EFFECTIVENESS OF VARIOUS CATALYSTS IN PROMOTING THE RATE OF REDUCTION OF UO_2F_2 AND UO_3[a]

		Time required for 50% reduction	
Catalyst	Catalyst no.	$UO_2F_2 \rightarrow UO_2$[b]	$UO_3 \rightarrow UO_2$[c]
None		25.0	10.0
Pt	1	7.0	1.5
Ru	3	5.5	3.0
Ir	4	6.5	3.4
Pd	6	6.0	2.0
Rh	7	5.0	1.8
Au	8	15.0	8.5
Ag	9	2.5	5.0
PdO_2	10	5.5	2.0
NiO	11	2.5	2.0

[a] The catalyst number refers to the catalysts listed in Table 2. For all catalyzed reductions, the catalyst concentration is 1.0 wt%.

[b] Reaction rates measured at 600°C.

Reaction rates measured at 550°C.

DISCUSSION

The present results suggest that in the course of both the oxidation and reduction reactions a reactive species which is formed on the catalyst surface can desorb and migrate considerable distances before reacting with the substrate. In the case of the reduction reactions, the reactive species are almost certainly hydrogen atoms, since the first excited state of the hydrogen molecule lies some 128 kcal above the ground state (7), and there is considerable other evidence (vide infra) that hydrogen atoms are formed on catalyst surfaces under the conditions used in the present work. While it would appear reasonable to suggest that a similar situation is occurring in the oxidation reactions, the participation of excited oxygen molecules, particularly the singlet $'\Delta$ state with an energy 23 kcal mole^{-1} above the ground state cannot be entirely excluded. The possibility of the formation of this species on catalyst surfaces has been suggested (*8*).

Extensive work (*1*a–c) has shown that in the reduction of WO_3 by H_2 at room temperature, the presence of water is crucial and that it provides an interface between the catalyst and substrate. It would seem unlikely, however, that water would occupy a similar role in the oxidation reaction. Our results on the reduction reactions could be interpreted in terms of previous observations (*9*) which showed that at temperatures near 400°C and pressures in the range of 30–60 cm, extensive dissociation of hydrogen into atoms occurs on the surface of supported platinum catalysts, and that these atoms are capable of migrating away from the platinum centers to the surface and possibly the interior of the catalyst support. This result would explain our observation that the reduction of UO_3 at 350°C is greatly enhanced when small amounts of platinum are deposited on the UO_3 surface. It will be recalled however, that at these temperatures the rate of reduction of the ADU–UO_3 could be only marginally increased by the addition of the supported catalyst, but that the rate of reduction of UO_2F_2 at temperatures near 600°C, and the reduction of the denitrator UO_3, near 550°C were strongly enhanced by the addition of the supported catalyst.

On the basis of these observations, we suggest that at low temperatures ($<450°C$) the hydrogen atoms produced on the platinum sites diffuse away from these sites largely by intraparticle diffusion, but that at higher temperatures interparticle diffusion becomes increasingly important. The results obtained for the experiments with the catalyst physically separated from the UF_4 indicate that at temperatures near 600°C at least some of the active oxygen species are able to leave the catalyst surface, and diffuse through the gas phase to the UF_4 surface where they react. It is interesting to note that a similar observation has been made previously by Gruenwald and Gordon (*10*), who showed that the heterogeneous exchange reaction between oxygen gas and solid, oxygen-containing substances such as Vycor, quartz and metal salts could be catalyzed by the presence of silver wire positioned near the solid surface. Preliminary experiments showed that in our system silver did not catalyze the oxidation of UF_4, possibly because the UF_6 produced reacted with the silver surface.

There have been several studies of the kinetics and mechanism of the atomization of hydrogen and oxygen on platinum surfaces (*11*) and these studies, which have been carried out at low gas pressures (10^{-2}–10^{-6} mm) and high temperatures (930–1530°C) showed that the activation energies of atomization for oxygen and hydrogen were 61.5 and 51.1 kcal mole^{-1}, respectively. The observation that the activation energies of both the oxidation and reduction reactions in the present study are in the range 24–30 kcal mole^{-1} suggests that the mechanism of the atomization is quite different under our experimental conditions, a conclusion not altogether unexpected in view of the very much higher gas pressures used in this work.

One surprising result of the present study is the observation that apparent activation energies of the oxidation and reduction reactions are unaffected by the presence of the catalyst and that the higher reaction rate of the catalyzed reactions is reflected in a higher preexponential factor of the Arrhenius equation. It has become an axiom of catalysis that the addition of a catalyst lowers the activation energy of the rate-determining step of a given reaction (*12*). It should be noted, however, that the present system is an unusual example of a catalytic effect in the sense that only one of the reactants (O_2 or H_2) can be adsorbed onto the catalyst surface. Furthermore, it is not possible to identify the step (or steps) to which the activation energy refers and which may include (a) the formation of the active species, (b) the reaction of the active species with the substrate, and (c) a diffusion controlled process, either with respect to the diffusion of the active species to the reaction site or the diffusion of reaction products from the reaction zone. If the formation of the active species is the rate-determining step in the reaction, the results imply that the activation energy for the atomization of either O_2 or H_2 is the same on a platinum or substrate surface but that, presumably because of an entropy effect (*13*), the total number of atoms produced in unit time and on unit surface area is much greater on the catalyst surface than on the UF_4 surface. As discussed in detail by Bond (*13*) this interpretation would make our observations an example of case IV of the compensation effect.

The details of the mechanism of the oxidation of UF_4 are very obscure at this time. Kirlis, McMillan and Bernhardt (*3*a) claimed to have isolated the compound U_2OF_8 from a reacting sample of UF_4 in O_2, but our attempts to reproduce this result invariably yielded UF_5. It seems likely, however, that some type of uranium oxyfluoride is an intermediate in this reaction and it is of interest to note that the compound UOF_4, which has recently been prepared and characterized (*14*), is reported to decompose to UF_6 and UO_2F_2 at temperatures near 400°C (*14*a).

It has been known for some time that certain metals, including platinum, will catalyze the oxidation of graphite (*15*). While there are superficial similarities between the results obtained in those studies and the results obtained for the oxidation of UF_4 in the present examination, the observation that a large variety of metals including lead, copper and cadmium are very effective catalysts for the oxidation of carbon but without effect on the oxidation of UF_4 suggests significant differences in the mechanisms operating in the two systems.

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