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Studies of Topochemical Heterogeneous Catalysis

2. Catalysts for the Reaction of UF_4 with Oxygen

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The reaction of oxygen gas with UF_4 according to the equation $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$ can be catalyzed by Pt, Ru, Ir, Os, Pd, Ag, Au and Co_3O_4, either supported on inert carriers or deposited directly on the UF_4. Catalyst activity was found to depend on the nature of the support, its surface area and particle size, and the concentration of metal on the support. The activation energy for the dissociative adsorption of oxygen is low on those metals and metal oxides which are effective catalysts. Variation in catalytic activity is attributable to differences in the entropy of oxygen adsorption on these surfaces, since the activation energies for the catalyzed reactions were found to be the same irrespective of the catalyst used.

INTRODUCTION

Recently we reported (*1*, *2*) details of what we believed to be the first example of a catalyzed oxidation reaction in which the rate of reaction of gaseous oxygen with a solid substrate is promoted by a solid catalyst. Such reactions have been termed topochemical heterogeneous catalytic reactions (*3*) and have previously been observed only in catalyzed reductions of metal oxides with hydrogen gas. Whereas in conventional heterogeneous catalysis, the catalyst acts as a third body on which the reaction of either two gases, two liquids, or a gas and a liquid can occur, in topochemical heterogeneous catalysis, the reaction does not occur on the catalyst. The catalyst instead acts as a surface for the activation of a gas to atoms or excited species which diffuse to the substrate surface before reacting.

In our example, the solid substrate, uranium tetrafluoride, was mechanically mixed with a supported platinum catalyst. On heating to 600°C in a stream of oxygen, gaseous UF_6 was evolved and solid uranyl fluoride remained.

$$2UF_{4(s)} + O_{2(g)} \xrightarrow[600°C]{\text{Catalyst}} UF_{6(g)} + UO_2F_{2(s)}.$$

Apart from its technological interest for the production of UF_6 by a method not requiring fluorine, this reaction is an interesting example of an unusual type of catalysis. This paper reports on a study of factors affecting the activity of catalysts for this reaction, including an examination of alternative catalysts which might offer some cost advantage over platinum. From these results it was hoped to obtain a better understanding of the nature of the catalytic process.

We have observed (*2*) that the reduction of both UO_3 and UO_2F_2 by hydrogen may be catalyzed in a similar manner to the UF_4–oxygen reaction and we are currently engaged in a comprehensive study of the topochemical heterogeneous catalysis of a number of analogous reduction and oxidation systems. Data obtained from these studies (*4*) have revealed many similarities in behavior between the oxidation and reduction reactions; the unique feature of such reactions is that the apparent activation energies of the catalyzed and uncatalyzed reactions are the same; the effect of the catalyst is to increase the value of the preexponential factor of the Arrhenius equation.

METHODS

Preparation of Catalysts

Supported noble metal catalysts were prepared by the following general method: a salt [$(NH_4)_2RhCl_6$, $(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, $RuCl_3$, $PdCl_2$, $AgNO_3$] or acid (H_2PtCl_6, $HAuCl_4$) of the metal was dissolved in water and slurried with the required weight of either UF_4 or inert support. This mixture was vibrated for 15 min in an ultrasonic bath, then evaporated to dryness using a rotary evaporator. The powder was dried in air at 100°C for 2 hr, then reduced in flowing hydrogen at 300°C for 3 hr. In the case of $PdCl_2$ dilute hydrochloric acid was added to dissolve the salt.

The transition metal oxides examined in this study were prepared by decomposition of a salt of the metal by heating in air at 500–800°C for 4 hr. The following salts (reagent grade) were used: the reaction temperatures are indicated in parentheses: $Co(NO_3)_2 \cdot 6H_2O$ (700°C), $CuSO_4 \cdot 5H_2O$ (800°C), NH_4VO_3 (500°C), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (600°C), $Fe(NO_3)_3 \cdot 9H_2O$ (600°C), $Ni(NO_3)_2 \cdot 6H_2O$ (600°C), $La(NO_3)_2 \cdot 3H_2O$ (600°C), $Zn(NO_3)_2 \cdot 6H_2O$ (600°C) and $Cd(NO_3)_2 \cdot 4H_2O$ (600°C).

Commercial samples of MnO_2, ZrO_2, HfO_2, Cr_2O_3, (from B.D.H. Chemicals Ltd) $PtO_2 \cdot xH_2O$ (Adam's catalyst) and PdO_2 (from Johnson Matthey Chemicals Ltd) were used.

Catalyst Supports

The following types of alumina were examined as support materials: α-Al_2O_3 (BDH Analar), Alcoa F1 activated alumina, Alcoa T61 tabular alumina, γ-alumina (Merck), Alcoa H151 alumina gel and a synthetic boehmite-derived γ-Al_2O_3. The last mentioned was prepared by the reaction of water with amalgamated aluminum (*5*), and dried in air at 600°C to convert it to a γ-alumina.

Reagent grade samples of calcium fluoride, barium sulfate, magnesium oxide and chromatographic silica were examined as alternative supports.

Uranium Tetrafluoride

Two different samples of uranium tetrafluoride were used in these studies. The first was a nuclear grade UF_4 supplied by E. Merck Australia Pty. Ltd. The other was prepared by reducing nuclear grade UO_3 prepared from ammonium diuranate in hydrogen at 500°C followed by hydrofluorination with anhydrous HF at 550°C. The only major impurities in this sample were Fe (100 ppm), Na (200 ppm), Mg (50 ppm), Co (20 ppm) and Si (20 ppm). Most work was performed on $-60 + 120$ mesh size fraction (150 to 250 μm), typical surface areas being in the range 1–2 $m^2\ g^{-1}$. Merck UF_4 had a surface area of 2 $m^2\ g^{-1}$, and a particle size less than 300 mesh (particle diameters approx 40 μm).

Reaction Rate Measurements

Reaction rates were measured on a Cahn thermobalance using 30 mg samples prepared by mechanically mixing catalyst and UF_4. Reactions were carried out at constant temperature measured by a Pt–Rh thermocouple suspended several millimeters from a gold sample pan and in a constant flow of nitrogen or oxygen dried by passage through two consecutive large traps containing activated molecular sieves.

RESULTS

The reaction between UF_4 and oxygen was found to be effectively catalyzed by platinum and a number of other metals and metal oxides (Fig. 1). For two reasons, we have been mainly concerned in these studies with reactions where the catalyst is deposited on an inert support, although as has been shown (*2*), a greater catalytic effect is observed if the catalyst is coated directly on the UF_4. Firstly, a reaction where catalyst and substrate are physically separated is obviously more applicable to any large scale production scheme for UF_6. Secondly, the fact that a catalytic reaction should proceed when solid catalyst is not in intimate contact with solid reactant was perhaps the most remarkable aspect of this work, and was obviously important to the understanding of the reaction mechanism.

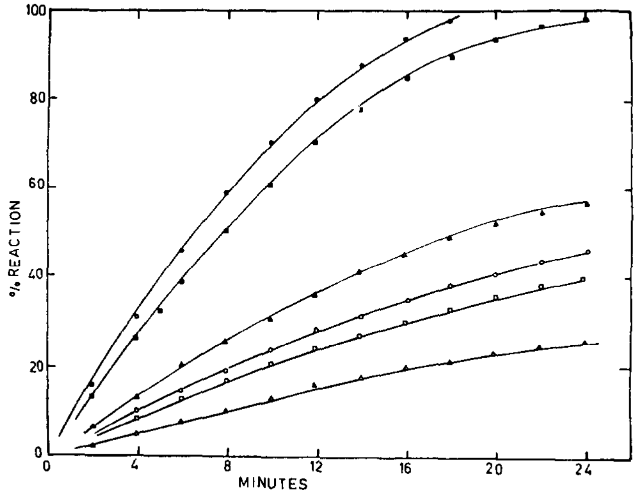

FIG. 1. Effect of various catalysts on the rate of oxidation of UF_4 at 640°C; catalyst concentration, 1 wt%: (●) 5% Pt on γ-Al_2O_3; (■) 5% Ru on γ-Al_2O_3; (▲) 5% Ir on γ-Al_2O_3; (○) 5% Os on γ-Al_2O_3; (□) 5% Pd on γ-Al_2O_3; (△) no catalyst.

It was considered that factors such as the type of support used, its surface area and particle size would affect the activity of the supported catalyst and the effects of these variables were examined in detail.

Study of Catalyst Supports

Table 1 shows the variation in the rate of reaction of UF_4 with oxygen in the presence of platinum supported on alumina having differing surface areas, as measured by BET nitrogen absorption. We have found it convenient throughout to express the reaction rate as $t_{1/2}$ the time for 50% of the UF_4 to react.

The data were obtained for supports of comparable particle size and show a direct correlation between surface area and activity. The apparent inconsistency in the results for the boehmite-derived catalyst arises from the fact that boehmite is formed by agglomeration of finer particles. Its structure is probably bidisperse, a microporous surface connected by a network of macropores which readily permit diffusion of active species.

As expected, the particle size of the catalyst was found to have a significant effect on its activity (Table 2). With a fine catalyst there is an increase in the proximity and number of catalyst particles around each UF_4 particle. Particle size is clearly as important as catalyst surface area in determining the rate of reaction.

In preparing the supported catalyst, conditions were chosen so as to give maximum dispersion of platinum on the support surface. These conditions have been well-defined in previous publications (*6–8*), where it was shown that reduction of supported chloroplatinic acid in flowing hydrogen at

TABLE 1

ACTIVITY OF ALUMINA SUPPORTED PLATINUM CATALYSTS AS A FUNCTION OF SURFACE AREA

Support	Surface area of support ($m^2\ g^{-1}$)	$t_{1/2}$ for Pt catalyst[a] (min)
Alcoa +61 tabular alumina 75–150 μm	0.04	>50
Merck γ-alumina 150–250 μm	90	42
Alcoa F1 activated alumina 150–250 μm	191	25
Boehmite-derived γ-Al_2O_3 150–250 μm	232	9
Alcoa H151 alumina gel 150–250 μm	298	12

[a] Catalysts prepared as 5 wt% platinum on support and tested as 1 wt% with UF_4 at 640°C.

TABLE 2
Effect of Platinum Catalyst Particle Size on Activity[a]

Particle size (μm) of support	$t_{1/2}$ (min)
40–75	6.5
75–150	10
150–250	12
200–400	13.5
Uncatalyzed	55

[a] 5 wt% Pt on H151 alumina gel tested as 1 wt% with UF_4 (75–150 μm) at 640°C.

TABLE 3
Activity of Platinum Catalysts Prepared on Different Supports[a]

Catalyst	Support	Particle size (μm)	$t_{1/2}$ (min)
5% Pt	SiO_2	<50	11
5% Pt	MgO	<50	25
5% Pt	$BaSO_4$	<50	25
5% Pt	CaF_2	<50	40
0.5% Pt[b]	CaF_2	<50	12

[a] Tested at 640°C, 1 wt% with UF_4 (75–150 μm).
[b] 10 wt% with UF_4.

temperatures near 350° gave the smallest platinum crystallites. Under these conditions, we obtained platinum crystallites of approximately 40 Å, as measured by X-ray line broadening.

In the oxidation of UF_4 using alumina-supported catalysts, an added complication arises because the gaseous reaction product UF_6 is adsorbed by alumina. This manifests itself in the thermogravimetric curve as an inhibition period followed by a weight loss, with the plateau indicative of complete reaction occurring at an apparent percentage reaction of less than 100%. The addition of uncovered alumina to the UF_4–catalyst mixture was used to demonstrate this feature (Fig. 2). Absorption can be minimized by ensuring that preparation conditions result in an even dispersion of small metal crystallites on the support. The absorptive capacity of alumina to UF_6 was also found to be reduced by pretreating the support with gaseous HF at room temperature. In all our experiments it was assumed that the absorption of UF_6 was negligible provided a stoichiometric weight loss was observed.

A number of alternative supports to alumina were examined (Table 3). Platinum catalysts prepared on these supports were generally inferior to alumina-based platinum catalysts as a result of the lower surface areas of these supports compared to that of alumina. However, by increasing the weight percentage of low activity catalysts in the reaction mixture, it was possible to

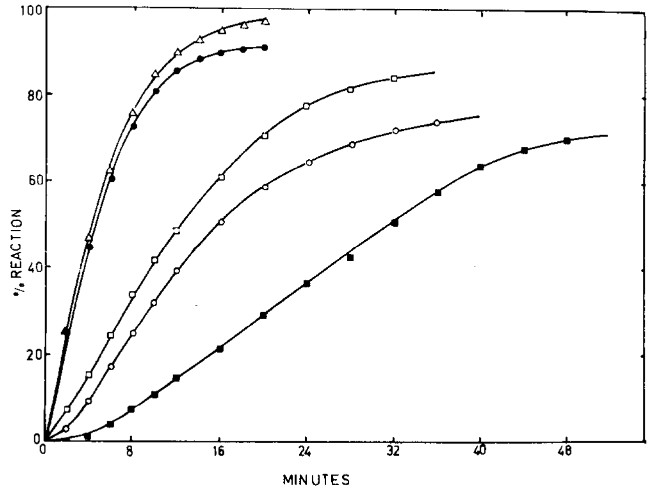

Fig. 2. Effect of uncovered alumina on the oxidation of UF_4 at 640°C in the presence of 1 wt% of the following: (△) 5% Pt on γ-Al_2O_3; (●) 5% Pt on γ-Al_2O_3 + 0.2% γ-Al_2O_3; (□) 5% Pt on γ-Al_2O_3 + 1% γ-Al_2O_3; (○) 5% Pt on γ-Al_2O_3 + 2% γ-Al_2O_3; (■) 5% Pt on γ-Al_2O_3 + 5% γ-Al_2O_3.

TABLE 4

Reaction of Platinum Coated UF_4 (5 wt%) with Oxygen

Temp (°C)	$t_{1/2}$ (min)
430	34
500	8
580	<2
580	>100 (no catalyst)

significantly increase the reaction rate. When the possibility of UF_6 absorption was eliminated by using nonabsorbing supports such as calcium fluoride, the weight of platinum on support could be reduced to 0.5 or even 0.1%. Table 3 shows that 10% by weight of a 0.5% platinum on calcium fluoride gave a reaction rate almost as fast as that for 1% by weight of a 5% platinum on alumina catalyst.

If the UF_4 is itself used as a base on which to deposit platinum, a minimum distance between catalyst and reactant is achieved and as anticipated the rate of reaction is now at a maximum. Table 4 shows that the oxidation of platinum coated UF_4 is catalyzed at temperatures as low as 430°C.

Unsupported Platinum Catalysts

The catalytic effect of platinum in differing forms and having greatly increased crystallite sizes is given in Table 5.

Catalysis by Metals Other than Platinum

A series of transition metals and transition metal oxides were examined as potential catalysts for the UF_4–oxygen reaction. Both alumina-supported and UF_4-supported catalysts were examined. In many cases it was not possible to decompose compounds to oxides on a UF_4 support without bringing about some reaction of the UF_4, thus limiting the number of UF_4-supported catalysts that could be examined. Table 6 lists these results. Catalytic activity was confined to the noble metals and other Group VIII metals and oxides namely Co_3O_4, Pt, Ru, Os, Ir, Rh, Au and Ag.

TABLE 5

Activity of Platinum Catalysts[a]

Catalyst	$t_{1/2}$ (min)
5% Pt on γ-Al_2O_3 (40–75 μm)	7
Pt black	9
Pt $O_2 \cdot xH_2O$ (Adam's catalyst)	14
Platinum metal filings	28
Uncatalyzed	50

[a] Tested at 640°C, 1 wt% with UF_4.

TABLE 6

Comparison of the Activity of Various Metal Catalysts in Promoting the Rate of Oxidation of UF_4

Catalyst conc (wt%)	Catalyst	Reaction temp (°C)	$t_{1/2}$ (min)
1	5% Pt on γ-Al_2O_3[a]	640	5
1	5% Ru on γ-Al_2O_3	640	8
1	5% Rh on γ-Al_2O_3	640	20
1	5% Ir on γ-Al_2O_3	640	20
1	5% Os on γ-Al_2O_3	640	27
1	5% Pd on γ-Al_2O_3	640	33
1	5% Au on γ-Al_2O_3	640	33
10	5% Au on γ-Al_2O_3	640	28
1	5% Ag on γ-Al_2O_3	640	50[b]
10	Co_3O_4 unsupported	640	10[b]
1	Co_3O_4 unsupported	640	29[b]
1	5% Pt on UF_4	597	12
1	5% Rh on UF_4	597	42
1	5% Ru on UF_4	597	65
1	5% Ir on UF_4	597	20
1	5% Os on UF_4	597	102
1	5% Pd on UF_4	597	64
1	5% Au on UF_4	597	67
1	5% Ag on UF_4	597	>100[b]
Uncatalyzed reaction		597	>100
		640	>50

[a] Boehmite derived γ-Al_2O_3 in each case.

[b] UF_6 absorption.

The following oxides were found not to exhibit any catalytic effect: MnO_2, CuO, V_2O_5, Fe_2O_3, ZrO_2, La_2O_3, HfO_2, Cr_2O_3 MoO_2, WO_3, ZnO, CdO and Ni_3O_4. Most of these were found to absorb or react with UF_6.

Discussion

The nature of the catalytic process may be inferred from a study of the manner in which such reactions depend on the physical nature of the catalyst. Boudart *et al.* (*9*, *10*) considered the classification of catalytic reactions as either demanding or facile; the former, requiring a special configuration of surface atoms, depend on the type of support and size of metal crystallites, while the latter class is independent of both factors. Slinkin and Federovskaya (*11*) have also provided a good summary of reaction types as a function of metal dispersion and carrier type.

From measurements of the reaction rate, we have obtained data for the catalytic reaction under varying conditions of catalyst preparation. The reaction rate was increased by increasing either the surface area of the catalyst support or the surface area of the catalyst metal. As an example of the latter, a change from platinum on γ-alumina to platinum metal filings which involves at least four orders of magnitude decrease in the dispersion of active sites (*9*) resulted in a significant decrease in reaction rate (Table 5). It would appear that the reaction may be classified, using Boudart's system (*10*), as a demanding reaction, although the lack of concise data concerning active metal surface areas and crystallographic states of the metal particles makes such a classification tenuous.

The observed increases in activity as a function of support surface area for platinum on alumina supports having the same density can be explained on the basis of increases in the dispersion of platinum as the surface area is increased. Changing the surface area of the support has an effect on the size of the platinum crystallites only when the surface becomes effectively covered with platinum at which point crystallite size will be decreased by either decreasing the support surface area or increasing the platinum concentration. Approximate calculations for a 5 wt% platinum on alumina catalyst having an alumina surface of 200 m^2 g^{-1} indicate that in this case platinum coverage approaches an atomic monolayer. X-Ray line broadening measurements showed that platinum crystallites on our catalysts had diameters of approximately 40 Å. Under these conditions, less than 5% of the alumina surface is covered with platinum. By coating UF_4 of surface area 2 m^2 g^{-1} with platinum, effective coverage of the surface of the UF_4 with 40 Å crystallites is achieved using a 5 wt% deposit. One would expect a decrease in activity on going to a platinum concentration giving less than complete coverage (e.g., 1% Pt) and this was indeed observed. If there is no change in platinum dispersion, it must therefore be assumed that decreasing the support surface area increases the concentration of platinum per unit surface, thus increasing the probability of some inhibiting reaction, such as atomic oxygen recombination occurring before the active species can leave the catalyst surface.

The above results show the strong dependence of catalytic activity on the surface properties of the catalyst, and lend support to the theory that the rate of reaction is controlled by the rate of formation of active species at the catalyst site. The role of diffusion of this species to the reaction site is also important, and we have shown that this occurs by both surface and gaseous diffusion, the former predominating at low temperatures. The closer the contact between the active species generating site and the reactant, the greater is the rate of reaction. For the same weight ratio of catalyst to UF_4, the rate is most rapid when the particle size of catalyst is smallest by comparison with UF_4, i.e., with greatest delocalization of active species generating sites. The limiting case is the uniform deposition of the catalyst on the surface of UF_4, where surface diffusion is the mode of active species transfer.

Of the many materials examined as potential catalysts, only the platinum metals, together with silver, gold and Co_3O_4 were found to catalyze the oxidation UF_4. The results of Boreskov (*12*) for the isotopic exchange of molecular oxygen on a series of metal and metal oxides have some bearing on our results. He proposed two mechanisms to fit the observed kinetics; the slow step in each case was the dissociative adsorption of oxygen. For oxygen exchange on platinum films at temperatures near 200°C and under 0.5 Torr pressure, his data per-

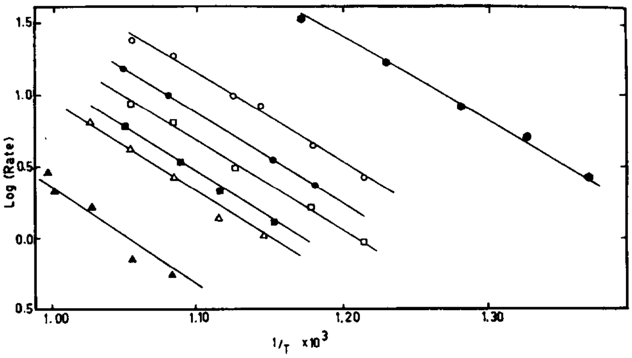

FIG. 3. Arrhenius plots for various catalyzed and uncatalyzed oxidations of UF_4: (▲) low surface area UF_4 (0.3 m^2 g^{-1}) no catalyst; (■) low surface area UF_4 (0.3 m^2 g^{-1}) + 1 wt% of 5% Ru on γ-Al_2O_3; (●) low surface area UF_4 (0.3 m^2 g^{-1}) + 1 wt% of 5% Pt on γ-Al_2O_3; (△) high surface area UF_4 (2.3 m^6 g^{-1}) no catalyst; (□) high surface area UF_4 (2.3 m^6 g^{-1}) + 1 wt% of 5% Ru on γ-Al_2O_3; (○) high surface area UF (2.3 m^6 g^{-1}) + 1 wt% of 5% Pt on γ-Al_2O_3; (◆) high surface area UF_4 (2.3 m^6 g^{-1}) coated with 1 wt% Pt^4

mitted the calculation of an activation energy for dissociative adsorption of oxygen of 23 kcal $mole^{-1}$. Those metals and metal oxides on which the exchange of molecular oxygen proceeded rapidly were those on which the exchange activation energy and the activation energy for dissociative adsorption is low. It is significant that the effective catalysts for the UF_4–oxygen reaction are those having approximately equal but low exchange activation energies, viz, Pt, Co_3O_4 and Ag, respectively, 16, 16.5 and 19 kcal $mole^{-1}$. No data were available for the other platinum metals, but those metal oxides such as V_2O_5, ZnO, MoO_3, Cr_2O_3 which did not exhibit catalytic activity in respect of the UF_4–oxygen reaction all had oxygen exchange activation energies significantly higher than 16 kcal $mole^{-1}$. Such oxides fall into a class distinguished by having high oxygen bonding energy and uniform surface oxygen, whereas Co_3O_4 has low oxygen bonding energy and nonuniform surface oxygen.

We have observed that the activation energies for both the catalyzed and uncatalyzed UF_4 oxidation reactions are the same, 23 ± 2 kcal $mole^{-1}$ (*2*). Irrespective of whether the rate controlling step is the dissociative adsorption of atomic oxygen or the excitation of molecular oxygen (the energy of the $'\Delta$ state is 23 kcal $mole^{-1}$ above the ground state) our results imply that UF_4 is itself a surface on which this reaction can occur although to date no data have been reported for oxygen exchange on UF_4.

Any differences in the activities of catalysts must therefore be attributed to differences in the entropies of adsorption which are manifested in the changing preexponential factors of the Arrhenius plots (Fig. 3). As expected the values of the preexponential factors were found to depend on the surface properties of both the UF_4 and the catalyst. Before any meaningful comparison of catalytic activities can be attempted, samples which are similar in surface properties, such as particle size, metal crystallite size and metal dispersion, must first be prepared.

Such differences are the likely cause of variations in the activity of UF_4-supported catalysts and in the same catalysts supported on alumina and mixed with UF_4 (Table 6). In addition any interaction of catalyst with UF_6 could tend to mask catalyst activity. Gruenwald and Gordon (*13*) reported results which indicate that silver should be an active catalyst, while our results indicate only moderate activity. A visual examination of a partly reacted UF_4 sample in the presence of a silver catalyst showed it to be fully reacted, the false rate curve resulting from absorption of or reaction with UF_6. To a lesser degree this effect was observed with Co_3O_4 catalyzed reactions.

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