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HETEROGENEOUS CATALYSIS IN FLUORIDE MELTS — REDUCTION OF URANIUM(V) BY HYDROGEN*

A. D. Kelmers and M. R. Bennett
Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

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Introduction

Solutions of pentavalent uranium are stable in fluoride melts contained in gold vessels (1). They are prepared by the reaction

$$UF_6(g) + UF_4(d) = 2\ UF_5(d),$$

where (g) and (d) represent the gaseous and dissolved states, respectively, in fluoride melts composed of LiF-BeF_2-ThF_4 (72-16-12 mole %), the fuel-carrier salt composition for the Molten-Salt Breeder Reactor (2). The reaction proceeds rapidly at 550-600°C and $UF_5(d)$ is stoichiometrically produced. The reduction of the pentavalent uranium to tetravalent uranium by hydrogen gas

$$UF_5(d) + 1/2\ H_2(g) = UF_4(d) + HF(g),$$

a necessary step in fuel reprocessing for the Molten-Salt Breeder Reactor, was reported (1) to proceed very slowly, however, and only a small fraction (<1%) of the hydrogen introduced was utilized.

This letter describes results which show that the hydrogen reduction reaction is rate limited, possibly due to the dissociation of hydrogen molecules to yield active hydrogen atoms, and reports the application of platinum catalysts to achieve a 10- to 100-fold increase in the reaction rate.

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Experimental

The experimental procedure, apparatus, chemicals and analytical methods used have been reported previously in detail (1). Briefly, for these experiments UF_5(d) was produced in molten LiF-BeF_2-ThF_4 (72-16-12 mole %) at 550°C by the stoichiometric reaction of UF_6(g) with UF_4(d). The melt was then sparged with hydrogen or hydrogen-argon gas mixtures at 550°C at 40 or 120 cc/min. Samples of the melt were taken periodically and analyzed by wet chemical techniques to determine the U(V) and U(IV) content.

Results and Discussion

The first series of tests at 550°C confirmed the low reaction rate between dissolved U(V) and gaseous hydrogen in the absence of a catalyst. Also, hydrogen utilization was low. The reduction followed zero-order kinetics (Figure 1), yielding a linear plot of moles of UF_5(d) reduced vs time. The quantity of UF_5(d) reduced was independent of the uranium concentration, hydrogen partial pressure or gas flow rate (mixing effects). The slope of the line yielded a rate constant, K, of 0.00135 mole/hr.

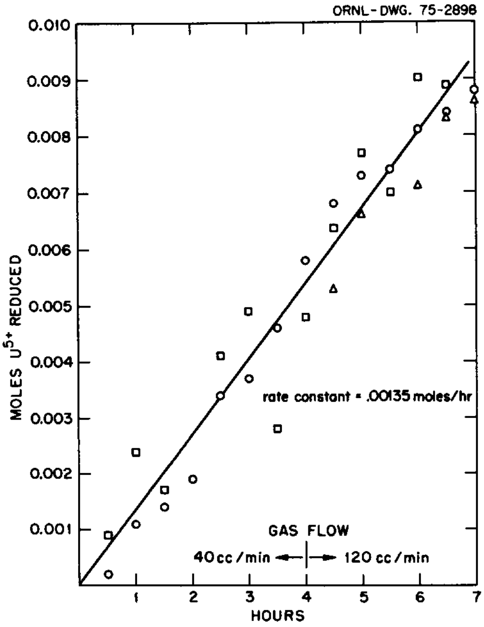

FIG. 1

Reduction of dissolved UF_5 at 550°C. Test 2, o, initial UF_5 concentration was 1.78 wt %, reducing gas was pure H_2. Test 5, □, initial UF_5 concentration was 4.60 wt %, reducing gas was pure H_2. Test 6, Δ, initial UF_5 concentration was 2.32 wt % and reducing gas was H_2-Ar (33-67 mole %).

The rate-limiting step may be the dissociation of the hydrogen molecule to active hydrogen atoms, H*, either on the surface of the gold vessel or dissolved in the melt. A possible simplified reaction sequence would be

$$H_2 = 2H^*$$

$$UF_{5+x}^{x-}\ (d) + H^* = UF_{4+y}^{y-}\ (d) + HF(d)$$

where the dissolved uranium species are represented as fluoride complexes. The dissolved form of U(IV) has been shown (3) to be UF_7^{3-} and UF_8^{4-}; the U(V) must be similarly complexed, although it has not been studied.

The effect of platinum catalysts, frequently used in petrochemical hydrogenation processes, was then investigated. An increase of 10- to 100-fold was achieved in the reaction rate for the reduction of U(V) (Table 1).

TABLE 1

Catalytic Reduction of Dissolved UF_5 by Hydrogen at 550°C

Run No.	Platinum Catalyst	H_2 Flow Rate (sccm)	Time (hr)	Initial U Conc. (wt %) Total U	Initial U Conc. (wt %) U^{5+}	U^{5+} Reduced (%)	H_2 Used (%)
8	Black[a]	0	0	3.92	2.56	0	
		40	0.5	3.86	<.05	100	20
11	Sponge[b]	0	0	5.24	4.08		
		0[c]	1.0[c]	5.18	4.18	0	
		0[c]	2.0[c]	5.26	4.14	0	
		40	0.25	5.66	0.96	66.8	
		40	0.5	5.40	0.14	96.6	31
		40	1.0	5.24	<.05	100	
12	Alloy[d]	0	0	2.18	1.96	0	
		0[c]	1.0[c]	2.28	1.64	0	
		0[c]	2.0[c]	2.37	1.90	0	
		40	0.5	2.41	<.05	100	15

[a] Granular (~100 mesh, 500 mg).

[b] Granular (45-65 mesh, 500 mg).

[c] Under argon.

[d] Small amount of Pt alloyed with or sintered to gold liner.

The order of the reaction could not be determined with the existing apparatus; the reaction proceeded almost to completion by the time the first sample was taken. The possibility that a reaction was occurring between the platinum and UF_5 to yield UF_4 or that the disproportionation reaction

$$2UF_5(d) = UF_4(d) + UF_6(g)$$

was being catalyzed to yield some UF_4 was precluded in run No. 11 (Table 1) in which the U(V) concentration was increased to 4.14 wt % and the solution was exposed to platinum for 2 hr in the absence of hydrogen. No reduction of U(V) occurred. Following introduction of the hydrogen, reduction was complete in about 30 minutes.

The physical form of the catalyst was not critical, either platinum black or granular platinum sponge was equally effective. In fact, trace amounts of platinum which alloyed with or sintered to the gold vessel during the first two experiments was equally active (run No. 12, Table 1). This suggests that it may be easy to take advantage of the catalytic effect in engineering-scale equipment by combining platinum with gold components of the apparatus.

The dissociation of the hydrogen molecule is possibly being accelerated on catalytic sites on the surface of the platinum. It is not known if the reaction occurs on the catalyst surface, in which case the rate-limiting step might be diffusion of species to or from the catalytic sites, or if association occurs between the hydrogen atom and some melt constituent to transport active hydrogen from the catalyst surface into the melt by some solvated species. Platinum was reported (4) not to catalyze the room temperature reaction between solid UF_6 and gaseous H_2 unless liquid HF was also present. This suggests the involvement of a solvated form of the active hydrogen atom. Platinum catalysts have been reported (5) to accelerate the reaction between solid UF_4 and O_2 gas, a diatomic molecule similar to H_2. Again dissociation to active atoms could be involved.

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