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

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Abstract

The reduction of uranium(V) or niobium(IV) dissolved in fluoride melts at 550°C by hydrogen gas in the absence of catalysts exhibits zero-order kinetics; i.e., the quantity reduced per unit time is independent of the concentration of dissolved species or the hydrogen gas partial pressure. Platinum catalysts accelerate the reaction rate 10- to 100-fold and, with uranium(V), the catalyzed reaction exhibits first-order kinetics suggesting that the catalyzed reaction may be diffusion limited. Platinum was catalytically active when present as platinum black powder, sponge, sheet or powder that had sintered to or alloyed with the gold reaction crucible.

Introduction

The fuel reprocessing scheme proposed for the Molten-Salt Breeder Reactor* involves the following steps for the recovery and recycle of the uranium fuel: (i) fluorination with \( \text{F}_2 \) gas to remove uranium as gaseous \( \text{UF}_6 \) from the molten fuel-carrier salt \( \text{LiF-BeF}_2-\text{ThF}_4 \) \((72-16-12 \text{ mole} \%\) containing fission products, (ii) reaction of the \( \text{UF}_6 \) gas with excess \( \text{UF}_4 \) dissolved in fresh molten fuel-carrier salt to produce dissolved \( \text{UF}_5 \), (iii) reduction of the dissolved \( \text{UF}_5 \) to \( \text{UF}_4 \) with hydrogen gas prior to recycle of the salt to the reactor. The reduction at 550°C of pentavalent uranium dissolved in \( \text{LiF-BeF}_2-\text{ThF}_4 \) \((72-16-12 \text{ mole} \%\) to tetravalent uranium by hydrogen gas proceeds via the reaction

\[
\text{UF}_5(d) + \frac{1}{2} \text{H}_2(g) = \text{UF}_4(d) + \text{HF}(g),
\]  

(1)

*Research sponsored by the Energy Research and Development Administration under contract with the Union Carbide Corporation.

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where (g) and (d) represent the gaseous and dissolved states, respectively. In addition to uranium, fission products that have volatile fluorides will be expected to be present in the hydrogen reduction step. Niobium is one of the major fission products and it should be volatilized as NbF₄ in the preceding fluorination step and then form soluble NbF₄ in the fluoride melt in this reduction reprocessing step. According to Baes², NbF₄(d) should be in equilibrium with Nb⁰; thus, the reaction with hydrogen gas at 550°C would be expected to be

\[ \text{NbF}_4(d) + 2\text{H}_2(g) = 4\text{HF}(g) + \text{Nb}^0. \]  

The reduction of uranium(V) dissolved in LiF-BeF₂-ThF₄ (72-16-12 mole %), Eq. (1), was reported³ to proceed very slowly at 550-650°C and only a small fraction (<1%) of the hydrogen was utilized. Similarly, the reaction of niobium(IV) with hydrogen, Eq. (2), was reported⁴ to be very slow at 700°C in molten Li₂BeF₄.

We have previously described⁵ results which show that the hydrogen reduction of uranium(V) is rate limited, possibly due to the dissociation of hydrogen molecules to yield active hydrogen atoms, and that platinum catalysts in various forms are effective in accelerating the reaction. In this report, the reaction order of the catalyzed reaction is described and the experimental work has been extended to include results with niobium.

**Experimental Methods**

The solvent salt, LiF-BeF₂-ThF₄ (72-16-12 mole %), and the high-purity UF₆ used in these experiments were prepared and purified by F. L. Daley and R. W. Horton of the ORNL Reactor Division by methods reported elsewhere.⁶ The UF₆ was shown by analysis to be greater than 99.9% pure. The hydrogen gas was generated electrolytically and passed through a palladium diffuser before use. The argon gas was purified by passage through a titanium sponge trap at 700°C to remove oxygen and hydrogen.

The apparatus and experimental techniques for the uranium(V) reduction reactions have been previously described.⁵ In a typical experiment, 200 g of solvent salt and the desired amount of UF₆ were charged to a 1.9-in.-diam by 8-in.-high gold liner (Fig. 1), which was then placed in a nickel containment vessel equipped with a gold gas sparge tube and a gold thermocouple well. The system was heated to 600°C and the molten salt was then sparged with HF-H₂ (50-50 mole %) to remove any residual traces of oxides or moisture. A predetermined amount of UF₆ gas, plus argon as a sweep gas, was added to the molten salt to prepare uranium(V) by the reaction

\[ \text{UF}_4(d) + \text{UF}_6(g) = 2\text{UF}_5(d). \]
The reaction proceeds rapidly at 600°C and UF₅(d) is stoichiometrically produced. To study the reduction of uranium(V) to uranium(IV), hydrogen or hydrogen-argon gas mixtures were then bubbled through the melt at 550°C. The melt was periodically sampled by opening the 0.5-in.-diam ball valve (Fig. 1) and inserting and promptly withdrawing a cold gold-tipped nickel sampler rod. The tip was covered with approximately 1 g of frozen salt which was quickly scraped into a vial (flooded with dry argon and then capped) and sent for analytical determination by wet chemical methods for uranium(V) and (IV) as previously described.

A similar series of tests was carried out with this apparatus to investigate the reduction of niobium(IV). Two hundred grams of solvent salt and 4 g of niobium metal chips were placed in the gold liner and hydrofluorinated at 600°C with anhydrous HF both to remove any impurity oxides from the salt and to generate dissolved NbF₅. To study the reduction of niobium, Eq. (2), hydrogen was then bubbled through the melt and the off-gas was scrubbed with buffer solution to trap HF, which was subsequently determined as fluoride ion by a specific ion electrode.

Results and Discussion

Reduction of Uranium(V)

The first series of tests at 550°C confirmed the low reaction rate and hydrogen utilization in the absence of a catalyst. The reduction followed zero-order kinetics as shown by the linear plot of moles of UF₅ reduced vs time which was independent of the uranium concentration, hydrogen partial pressure or mixing effects due to gas flow rate (Fig. 2). The rate constant was 1.35 mmoles/hr.

Zero-order kinetics are consistent with the postulated rate-limiting step being the dissociation of hydrogen molecules to yield active hydrogen atoms, H*,

$$H_2 = 2H^*.$$  (4)

This could be taking place either on the surface of the gold liner or in the melt. The active hydrogen atoms then react with the dissolved uranium species

$$UF_{5+x}^-(d) + H^* = UF_{n+y}^{V+}(d) + HF,$$  (5)

where the dissolved species are represented as fluoride complexes. The dissolved form of uranium(IV) has been shown to be a mixture of UF₇³⁺ and UF₈⁴⁺; the uranium(V) must be similarly complexed but, since it has not been studied, the value of x is not known.
Platinum catalysts in four different forms were then investigated. An increase of 10- to 100-fold was experienced for the rate of reduction of uranium(V) (Table 1). In each case, essentially complete reduction occurred usually in 0.5 hr or less, and the order of the catalytic reaction could not be determined. The possibility that a chemical reaction was occurring between the uranium(V) and platinum was precluded by the results of the sponge and alloy experiments (Table 1). No reduction of uranium occurred when the solution was exposed to the platinum for 2 hr in the absence of hydrogen.

The physical form of the catalyst was not critical; platinum black powder, granular platinum sponge or platinum sheet were active. In fact, trace amounts of platinum which alloyed with or sintered to the gold vessel in the tests with platinum black or sponge were also active. This unanticipated finding was encouraging for practical applications since it suggested that only small quantities (or limited available surface area) may be required; however, it rendered this gold liner useless for further tests. A new gold liner was employed in the test with a platinum disk, surface area 8.6 cm$^2$, prepared by pressing a platinum sheet into a gold disk so that a smooth surface of defined area could be obtained.

To investigate the kinetics of the catalyzed reaction, two tests were carried out by placing a gold disk containing an inserted platinum disk with a surface area of 8.6 cm$^2$ in the bottom of a new, non-catalytic, gold liner. Hydrogen was introduced at 10 or 20 cc/min and samples were taken at 10- or 15-min intervals. The resulting data, when normalized and plotted as ln $[U_5^+]/[U_5^+]$ vs time (Fig. 3), gave a straight line, suggesting first-order kinetics for the catalyzed reaction with a half-life of 65 min. First-order kinetics might be expected for a reaction that is diffusion limited. The rate-limiting step could be diffusion of uranium(V) from the stirred melt to the catalyst surface or diffusion of the uranium(IV) or an active intermediate from the catalyst surface. A solvated species could be involved since platinum has been reported not to catalyze the room temperature reaction between solid UF$_6$ and gaseous H$_2$, unless liquid HF was present. "Spillover" of active hydrogen from platinum catalysts to inert supports has been observed in other systems and could be a factor here; thus, it is important to test this system to determine its response to changes in catalytic area. Additional tests are also planned to evaluate the effect of hydrogen partial pressure to see if the reaction is pseudo first-order due to an excess of hydrogen in these first tests.

Reduction of Niobium(IV)

A series of tests was carried out with melts containing 0.33 to 1.1 wt % niobium(IV) at 550°C which were sparged with hydrogen at 40 cc/min. The reduction reaction, Eq. (2), proceeded very slowly. After normalization to correct for a surge of HF generated when
hydrogen was initially admitted to the system, the data (Fig. 4) yielded a single line when plotted in the form for zero-order kinetics with a rate constant of 0.208 mmole Nb/hr. Thus, the reduction of niobium(IV) is similar to that of uranium(V); whether this is a general characteristic for the hydrogen reduction of fluoride-complexed ions in melts of this type remains to be established. Certain reactions could be autocatalytic; the rapid reduction of nickel(II) by gaseous hydrogen may be an example of such a case.

In one niobium(IV) reduction test with granular platinum sponge present, the rate of generation of HF was accelerated for the first 2 hr and then decreased to a value similar to that experienced in the uncatalyzed reactions. The quantity of HF evolved during the first 2 hr was equivalent to that for the reaction

\[ \text{NbF}_4(d) + 1/2 \text{H}_2(g) = \text{NbF}_3(d) + \text{HF}(g). \]  

Possibly a species in an intermediate oxidation state, such as NbF3, may be metastable and offer a kinetic barrier to the complete reduction to niobium metal. Conversely, the platinum catalyst may have been poisoned by the reaction products and lost its activity. Thus, the apparent generation of HF equivalent to reduction to Nb(III) may be coincidental. Additional experimental work is needed to unequivocally establish the reduction reaction and kinetic order.

Acknowledgements

The authors wish to acknowledge the services of ORNL Analytical Chemistry Division personnel under the supervision of W. R. Laing, and thank C. E. Bamberger, ORNL Chemistry Division, for supplying the platinum black.

References

1. L. E. McNeese and M. W. Rosenthal, Nuclear News 17, 52 (Sept. 1974).
2. C. F. Baes, Jr., J. Nucl. Mater. 51, 149 (1974).
3. M. R. Bennett and L. M. Ferris, J. Inorg. Nucl. Chem. 36, 1285 (1974).
4. C. F. Weaver and J. S. Gill, MSR Program Semiannual. Prog. Rep. Feb. 28, 1971, ORNL-4676, p. 85.
5. A. D. Kelmers and M. R. Bennett, Inorg. Nucl. Chem. Lett. 12, 333 (1976).
6. J. H. Shaffer et al., Reactor Chem. Div. Annu. Prog. Rep. Jan. 31, 1964, ORNL-3591.
7. L. M. Toth, J. Phys. Chem. 75, 631 (1971).
8. J. H. Levy and P. W. Wilson, Aust. J. Chem. 26, 2711 (1973).

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9. R. B. Levy and M. Boudart, J. Catalysis 32, 304 (1974).
10. G. E. E. Gardes, G. M. Pajonk and S. J. Teichner, J. Catalysis 32, 145 (1974).
Table 1. Catalytic Reduction of Uranium(V) by Hydrogen at 550°C

| Platinum Catalyst | H₂ Flow Rate (cc/min) | Time (hr) | U⁵⁺ Concentration (wt %) | U⁵⁺ Reduced (%) | H₂ Utilization (%) |
|-------------------|-----------------------|-----------|--------------------------|----------------|-------------------|
| Black² | 0 | 0 | 2.56 | 0 | — |
| | 40 | 0.5 | <0.05 | 100 | 20 |
| Sponge³ | 0 | 0 | 4.08 | 0 | — |
| | 0 | 1.0 | 4.18 | 0 | — |
| | 0 | 2.0 | 4.14 | 0 | — |
| | 40 | 0.25 | 0.96 | 67 | — |
| | 40 | 0.5 | 0.14 | 97 | 31 |
| | 40 | 1.0 | <0.05 | 100 | — |
| Alloy⁴ | 0 | 0 | 1.96 | 0 | — |
| | 0 | 2.0 | 1.90 | 0 | — |
| | 40 | 0.5 | <0.05 | 100 | 15 |
| Sheet⁵ | 0 | 0 | 2.00 | 0 | — |
| | 10 | 2 | <0.05 | 100 | 8 |

²500 mg platinum black, ~100 mesh, surface area 9.8 m²/g
³500 mg platinum sponge, 45-65 mesh, surface area ~0.1 m²/g
⁴Held under argon atmosphere
⁵Small amount of platinum alloyed with or sintered to the gold liner
⁶⅛ in.-thick platinum sheet pressed into 1.75-in.-diam gold disk, platinum superficial surface area 8.6 cm². New gold liner for this test.
Fig. 1. Photograph of the nickel containment vessel with gold liner, sparge tube and thermocouple well and ball-valve access for sampling.
Fig. 2. Reduction of Uranium(V) at 550°C.

| Symbol | Initial UF₆ (wt %) | Sparge Gas       |
|--------|--------------------|-------------------|
| o      | 1.75               | H₂                |
| □      | 4.60               | H₂                |
| △      | 2.32               | H₂-Ar (33-67 mole %) |
Fig. 3. Catalytic Reduction of Uranium(V) at 550°C.

| Symbol | Initial UF₆ (wt %) | Sparge Gas |
|--------|-------------------|------------|
| ○      | 2.06              | H₂         |
| •      | 3.54              | H₂         |
Fig. 4. Reduction of Niobium(IV) at 550°C.

| Symbol | Initial NbF$_4$ (wt %) | Sparge Gas          |
|--------|------------------------|---------------------|
| ○      | 1.1                    | H$_2$               |
| □      | 0.92                   | H$_2$-Ar (30-70 mole %) |
| □      | 0.33                   | H$_2$               |
| □      | 0.72                   | H$_2$               |