CATALYTIC EFFECT OF FISSION PRODUCTS ON THE LOW TEMPERATURE FLUORINATION OF URANIUM OXIDE WITH ELEMENTAL FLUORINE

M. MAEDA and E. YAGI^{*} Division of Nuclear Fuel Research, Japan Atomic Energy Research Institute, Tokai, Japan

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Introduction

Fluorination of uranium oxides with elemental fluorine has practical significances as a basic reaction in the fluoride volatility process (FVP), an advanced non-aqueous reprocessing process.

However, little attentions have been paid to the effect of fission products on the fluorination rate of uranium. Two reports only provide material for the discussion. Whereas no significant effect is shown in the results by Henrion and Leurs (1), data obtained in engineering scale experiments at Argonne National Laboratory (2) reveal considerable acceleration effect of fission products, although the authors explain it as due to the different history of the powder prepared. Similar facts were also observed in the fluorination of mixed $PuO_2^ UO_2$ powder with fluidized bed (3).

In this letter we report a marked enhancing effect of fluorination rate by small quantities of non-valatile elements added to uranium oxide powder as simulated fission products. This effect would be of interests for the possible application to the catalytic conversion of uranium oxides under low temperature below 300 °C and for a new example of the unusual topochemical effect (4) in fluorination.

Preparation of simulated fission products

Two kinds of simulated fission products (SFP) mixture are prepared; one fully simulated for the spent fuel of LMFBR core with 100 MWd/kg burn-up (5) (FP-I) and another of simplified simulation composition shown in Table 1 (FP-II). The elements in the table were selected from major fission products that do not form volatile fluorides and their compositions were adjusted so that each element selected represents total composition of the fission products belonging to the same group of periodical table. These SFP's which were originally oxides with spectroscopic grade purity, were mixed mechanically after pulverizing into fine powders and fluorinated under 450 ~ 550 °C and 50 vol. $% F_2$ -N₂ for 5 hrs in advance to mixing with UO₂ powder for experiments.

* Present address, Mitsubishi Metal Corp Inc., Tokyo, Japan.

Original Chemical Form	Composition	Added as substitute for
CeO ₂	55.4 w/o	Lanthanide elements
PdO	33.0	Ru, Rh etc.
Ag ₂ 0	7.6	Cs, Rb, Sr, Cd etc.
Sn0 ₂	2,3	Zr etc.
sb ₂ 0 ₃	1,8	Nb etc.

 TABLE 1

 Compositions of Simulated Fission Products (FP-II)

Experimentals

 $\rm UO_2$ used were prepared by mechanically pulverizing reactor-grade pellet of Furukawa Kogyo Co. Ltd. The specific surface area measured by BET with Kr was 0.9 m²/g. Mixing of simulated fission product fluorides with $\rm UO_2$ were made by mechanically shaking. Reaction rates were measured gravimetrically with a thermobalance using 25 ~ 40 mg samples on a pan suspended in a reactor of monel with 30 mm diameter and 130 mm length. Fluorine from Air Product Co. was used after passing it through a NaF loaded column to remove HF impurity and diluting it with highly purified nitrogen gas. All experiments were conducted under atmospheric pressure with a fixed total gas flow of 300 ml/min (STP).

Results and discussion

In order to make SFP's effect clear, experiments were conducted using UO₂ with and without their addition. Marked acceleration effects of SFP on fluorination rate are shown in Fig. 1, where cubic root of unreacted fraction to initial sample weight, $(1-F)^{1/3}$, are plotted against reaction time t correlating by the diminishing sphere model (6). The result indicates that the effect depends considerably on concentration of SFP added and also that simplified simulation mixture FP-II is more effective than fully simulated FP-I.

Diminishing sphere model derives an equation of $(1-F)^{1/3} = 1-k't$, where k' is an apparent reaction rate constant. Therefore, the slope in the figure provides this k'. Fig. 2 shows Arrhenius plot of k', comparing with that of pure UO_2 . Table 2 summerizes major kinetic characteristics obtained on samples with and without SFP. Present auther's results without SFP addition show good agreements with data reported by other investigators (10, 11, 12). Activation energy and reaction order with fluorine for SFP-added reaction were found to be almost identical with those for non SFP-added fluorination. Only major difference is pre-exponential factor of Arrhenius equation, 10^2 to 10^3 times larger when SFP added.

Since added SFP was thoroughly fluorinated under more intense condition before mixing with UO₂ and its quantities added are sufficiently small, physical effect due to the heat of SFP's fluorination will be ignorable. Hence, this strong acceleration effect could be due to some chemical mechanism, although



FIG. 1

Effect of Simulated Fission Products on Fluorination Rate of ${\rm UO}_2.$

Temperature, 280°C. Fluorine, 4.8 vol. %. UO₂ used, 40 mg.

effective elements were not identified. Similar examples are reported on reduction of metals with hydrogen (4) and oxidation of UO_2F_2 to form UF_6 (7), where palladium and platinum are found to have intense catalytic effect and also, in the latter, activation energy in the catalyzed reaction are identical with that in non-catalyzed one. An example on catalytic fluorination of UO_2 is reported, though the catalyst is gaseous bromine (9).

Generally, elemental fluorine requires higher temperature to fluorinate UO₂ than interhalogens such as BrF_3 , BrF_5 and $C1F_3$, probably because of larger dissociation energy of F-F bond (8). Since the probability that both reacting solid and gas are adsorbed simultaneously on the catalyst is small because of the very low concentration of catalysts and their limmited migration distance, one presumable mechanism might be that catalysts facilitate dissociation of fluorine and/or its adsorption onto UO₂ or UO₂F₂. In this mechanism, the same effect might be expected in the fluorination of UF₄, suggesting its possible



application to improvement of fluorine utilization in conversion process for UF_6 production.

FIG. 2

Fluorination Rate Constant of UO $_2$ with and without Addition of Simulated Fission Products, correlated by Diminishing Sphere Model.

 UO_2 used 40 mg. Data correlated to the condition of unit F_2 concentration.

TABLE 2

Summary of Kinetics in Catalyzed and Non-catalyzed Fluorination, Correlated by Diminishing Sphere Model.

Reactions	Catalyzed	Non-catalyzed
Activation energy	29 Kcal/mol	28 Kcal/mol
Reaction order of fluorine concentration	0.69	1.0
Pre-exponential factor of Arrhenius equation	$2.0 \times 10^9 \text{ min}^{-1}(1.1 \text{ w/o SFP})$ 1.6×10^{10} (12 w/o SFP)	$3.5 \times 10^7 \text{ min}^{-1}$

The present results indicate the fluorination behavior of irradiated or SFP added UO_2 should be evaluated carefully without directly extrapolating the data on pure UO_2 . The same catalytic effect was confirmed in scaled-up experiments using fluidized-bed, of which detailed results will be soon published.

References

- 1. P.N.HENRION and A.LEURS, J. Nucl. Materials, <u>41</u>, 1 (1971).
- L.J.ANASTASIA, P.G.ALFREDSON, M.J.STEINDLER, G.W.REDDING, J.G.RIHA and M.HAAS, USAEC Report ANL-7372 (1968).
- 3. Fuel Reprocessing Laboratory's staff in Japan Atomic Energy Research Institute, JAERI-M 6393 (1976).
- 4. N.I.IL'CHENKO, Russ. Chem. Rev., 41, 47 (1972).
- 5. N.M.LEVITZ, USAEC Report ANL-7583 (1969).
- 6. V.Y.LABATON and K.D.B.JOHNSON, J. Inorg. Nucl. Chem., <u>10</u>, 74 (1959).
- 7. A.EKSTROM and G.E.BATLEY, Inorg. Nucl. Chem. Letters, 9, 1157 (1973).
- 8. T.SAKURAI, J. Phys. Chem., <u>78</u>, 1140 (1974).
- 9. T.SAKURAI, J. Nucl. Sci. & Tech., 12, 308 (1975).
- 10. M.IWASAKI, J. Inorg. Nucl. Chem., <u>26</u>, 1853 (1964).
- 11. G.VANDEN BUSSCHE, CEA-R 2859 (1977).
- 12. R.L.JARRY, ANL-6763 (1963).