Investigation of the Kinetics of U_3O_8 Reduction by Hydrogen and Ammonia under Non-Isothermal Conditions

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Abstract

The possibility of preliminary reduction of U_3O_8 with hydrogen and ammonia before its fluorination for the purpose of increasing uranium (IV) content in the product is considered. Results of the investigation aimed at the determination of optimal temperatures and the kinetics of U_3O_8 reduction under non-isothermal conditions by means of temperature-programmed reduction are presented.

Key words: triuranium octoxide, reduction, hydrogen, ammonia, uranium dioxide, temperature, kinetics, non-isothermal conditions

INTRODUCTION

Oxygen compounds of uranium or uranium oxides such as uranium dioxide UO_2, uranium trioxide UO_3 and triuranium octoxide U_3O_8 play an important role in the technology of nuclear fuel. But perhaps even more important they are as intermediate products in the production technology of other uranium compounds, mainly fluorides (uranium tetra- and hexafluoride) [1].

Studies performed earlier demonstrated the basic potentiality of realizing the process of hydrofluorination in sublimate production. The use of anhydrous hydrogen fluoride as a fluorinating agent produces allows obtaining uranium oxyfluorides with fluorine content ranging within 15−16 % *via* the hydrofluorination of U_3O_8. The fluorination of a hydrofluorinated product in the flame reactor could result in reducing the specific consumption of fluorine per unit product to increase the productivity of the technological process with respect to uranium hexafluoride [1].

The use of uranium oxide with a high content of uranium (IV) at the stage of hydro-fluorination could result in increasing the fluorine content in the product obtained. Increasing the amount of uranium (IV) could be achieved by means of the reduction of hexavalence uranium (in the form of UO_3 or U_3O_8) by different reducing agents, such as hydrogen, ammonia, *etc.* [2].

Under laboratory conditions, we studied the process of obtaining uranium oxides with a high content of uranium (IV), where hydrogen gas and ammonia are used as a reducing agent.

For the calculation of the kinetic parameters for U_3O_8 reduction by hydrogen and ammonia, we have chosen a method described in [3] based on displacing the maximum temperature at different heating rates. This method is a differential one and the best in our conditions, since the reduction of uranium oxide consists of a set of elementary stages, whose contribution varies as the process proceeds. Application of integral methods [4] is problematic, since the use of integral characteristics could be connected with some uncertainty caused by a non-stoichiometricity of the composition of $U_3O_{(8 \pm x)}$.
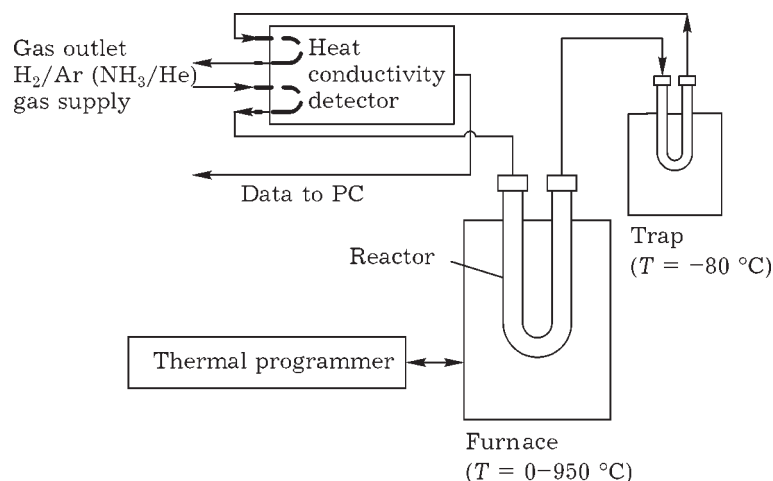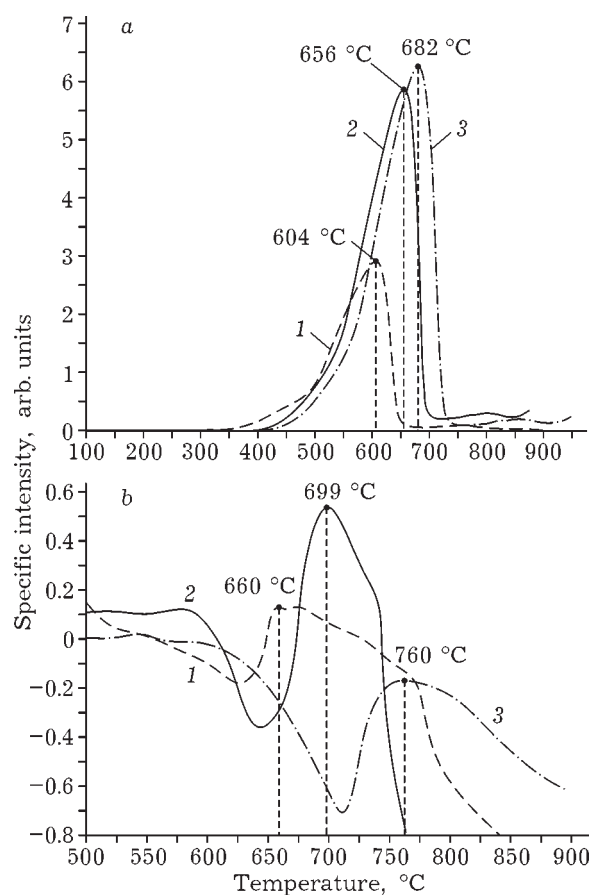
Fig. 1. Schematic diagram of Chemisorb 2750.

EXPERIMENTAL

For the experiments we used U_3O_8 weighed samples with the mass ranging within 0.1–0.25 g, with the bulk density of 2.7–3.1 g/cm^3 and the specific surface area of 0.3–0.4 m^2/g. The specific surface of the product was determined by means of BET technique, tapped the bulk density was determined by means of tapping method.

The experiments were performed in a gas-mixture environment such as H_2/Ar and NH_3/He. Both hydrogen and ammonia in the mixture amounted to 10 %.

The U_3O_8 reduction kinetics investigation was carried out using the Chemisorb 2750 unit (Micromeritics, USA), whose schematic diagram is demonstrated in Fig. 1.

Monitoring the reduction process was carried out using a thermal conductivity detector of Chemisorb 2750 unit. In order to eliminate the contribution of water formed and released due to the reaction to the thermal conductivity of the gas mixture the vapour was frozen in a trap cooled by frozen isopropyl alcohol. When reducing U_3O_8 by ammonia, freezing water vapour was not carried out, since this procedure would result in freezing ammonia, too, thus as a consequence, in a greater measurement error with respect to the gas system thermal conductivity and the kinetic curves obtained.
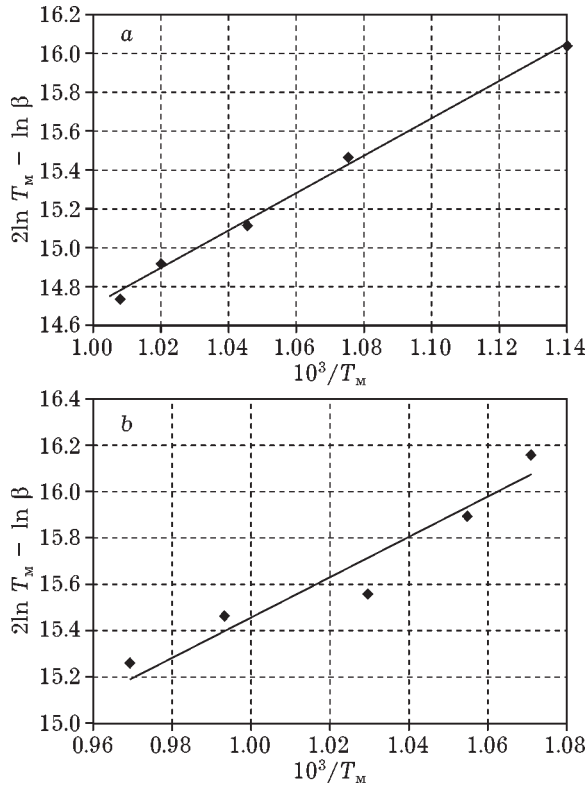

Fig. 2. Differential isothermal kinetic curves for hydrogen reduction (*a*) and ammonia (*b*) reduction of U_3O_8. The rate of heating the samples, K/min: 5 (*1*), 10 (*2*), 15 (*3*).

Fig. 3. Determination of the activation energy and pre-exponential factor for the reduction of U_3O_8 by means of hydrogen (*a*) and ammonia (*b*).

RESULTS AND DISCUSSION

For correct determining the kinetic parameters of the reduction process we have chosen five settings for the heating rate: 5, 10, 15, 20 and 25 K/min. As the result, we obtained the following temperature values corresponding to the maximum rate of the process: 1) for the gas mixture H_2/Ar they are 604.0, 656.3, 682.2, 707.1 and 725.6 °C, respectively, and 2) for the gas mixture NH_3/He they are 660.0, 699.0, 760.0, 797.1, 846.4 °C, respectively.

In order to avoid interference and for a greater clarity, Fig. 2 demonstrates only three differential kinetic curves for the reduction of U_3O_8, corresponding to the first three heating rates (5, 10, and 15 K/min). In Fig. 2 the specific intensity of the signal strength should be understood as the signal intensity of thermal conductivity detector, reduced to unit mass of U_3O_8 sample.

According to [5], metal oxide reduction processes occurring under non-isothermal conditions could be described by the following kinetic equation:

$$\frac{d\alpha}{d\tau} = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \qquad (1)$$

where α is the conversion level, %; τ is time, s; A is the pre-exponential factor, min^{-1}; E_a is the activation energy, J/mol; T is the thermodynamic temperature, K; R is the gas constant, J/(mol · K); n is the kinetic order of the process.

At the time of the maximum rate of the process, the eq. (1) possesses the following form

$$\frac{d}{dT}\left[\frac{d\alpha}{d\tau}\right] = \frac{d}{dT}\left[\frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n\right] \qquad (2)$$

where β is the rate of heating the sample, K/min.

For a first-order reaction ($n = 1$), we obtain the following expression:

$$2\ln T_m - \ln\beta = \frac{E_a}{RT_m} + \ln\frac{E_a}{AR} \qquad (3)$$

where T_m is the temperature of maximum reaction rate, K.

Basing on equation (3) we determined the activation energy from the line slope for coordinates: $2\ln T_m - \ln\beta = f(10^3/T_m)$, and the pre-exponential factor was determined from the intercept with the vertical axis (Fig. 3).

The kinetic characteristics of U_3O_8 reduction by hydrogen and ammonia exhibit the following values: in the case of hydrogen (H_2/Ar mixture) $E_a = (81.6 \pm 6)$ kJ/mol, $A = (76.77 \pm 4)$ min^{-1}, in the case of NH_3/He mixture $E_a = (69.5 \pm 14)$ kJ/mol, $A = (7.02 \pm 2)$ min^{-1}.

TABLE 1

Results of kinetic calculations for U_3O_8 reduction by hydrogen and ammonia

β, K/min	Temperature of maximum rate, °C	
	Calculated	Experimental
	Reducing agent − H₂/Ar	
5	605.0	604.0
10	655.0	656.3
15	684.0	682.2
20	707.0	707.1
25	725.0	725.6
	Reducing agent − NH₃/He	
5	650.0	660.0
10	711.0	699.0
15	749.0	760.0
20	771.3	797.1
25	807.8	846.4

TABLE 2

Reduction parameters and product compositions
for the reduction of U_3O_8 by hydrogen and ammonia

β,	Mass fraction, %		$\alpha^{U(6+) \to U(4+)}$,	T_m,	τ,
K/min	U_{total}	U^{4+}	%	°C	min
	Reducing agent − H_2/Ar				
5	86.67	81.71	89.33	604.0	58.6
10	86.0	78.50	83.97	656.3	29.1
15	85.60	70.24	70.18	682.2	21.6
20	85.40	67.50	65.60	707.1	16.3
25	85.29	65.60	62.43	725.6	12.5
	Reducing agent − NH_3/He				
5	86.46	80.56	87.41	660.0	31.5
10	85.75	79.00	84.81	699.0	10.3
15	86.20	78.10	83.31	760.0	7.2
20	85.95	76.55	80.72	797.1	5.1
25	85.82	74.03	76.51	846.4	3.8

To verify the consistency of the calculated values of the kinetic parameters with the experimental numerical values, basing on equation (3) we obtained the following equation [5]:

$$\frac{E_a}{RT_m} = \ln\frac{A}{\beta} - \ln\left(\frac{E_a}{RT_m}\frac{1}{T_m}\right) + \ln\left[n(1-\alpha)^{n-1}\right] \quad (4)$$

The resulting transcendental equation was solved with respect to T_m using the Maple 10 software.

The results of kinetic calculations are presented in Table 1.

One can see that in the case of reduction of U_3O_8 sample in a flow of H_2/Ar at different heating rates the calculated data agree to a high accuracy with the experimental data to indicate that the selected kinetic model chosen is quite adequate within this temperature range.

However, for the reduction of U_3O_8 sample in NH_3/He medium the calculations according to first order kinetic equations result in the fact that the temperature values calculated are in a significant disagreement with the experimental data. Thus, the kinetic characteristics obtained represent, to all appearance, some effective estimates those do not reflect true kinetic patterns which could be used for technological calculations.

The samples of U_3O_8, reduced by hydrogen and ammonia at different heating rates were subjected to chemical analysis in order to determine the content of tetravalent uranium, total uranium and the level of the product reduction (Table 2).

As it follows from Table 2, in the case when H_2/Ar gas mixture is used, the level of reduction for U_3O_8 sample is higher than in the case of using NH_3/H_2 gas mixture; this value reaches 89.33 % at a heating rate about 5 K/min. In this case, the maximum temperature was 604 °C. However reducing the sample by means of H_2/Ar mixture requires much more time.

With increasing the heating rate of U_3O_8 sample in both cases (reduction by hydrogen and by ammonia), a shift of peak temperature values is observed towards a higher temperature range which, consequently, results in decreasing the product reduction level. However, when $\beta = 5$ and 10 K/min, a fairly complete reduction of U_3O_8 sample is observed. The U^{4+} content therein after the experiments increased from 32−33 to 80−90 %, thereby it can be used for the further hydrofluorination.

CONCLUSION

From the results of the studies on the reduction of U_3O_8 by hydrogen and ammonia in the temperature-programmed heating unit one can draw the following conclusions:

1. The process of U_3O_8 reduction by hydrogen begins at temperature values above 350 °C, whereas as the temperature increases the rate of U_3O_8 reduction increases, too;

2. The U_3O_8 ammonia reduction process takes place at higher temperature values and stages-by-stage. To all appearance, the first stage is the decomposition of ammonia at the temperature values of 500−630 °C, and then reducing the U_3O_8 sample occurs at the temperature values ranging within 630−700 °C;

3. The increase in the heating rate of U_3O_8 samples from 5 to 25 K/min results increasing the temperature where the maximum rate of reduction by both hydrogen, and ammonia;

4 The values of activation energy and pre-exponential factors for the processes of U_3O_8 reduction by hydrogen and ammonia calculated according to the methods designed for non-isothermal processes are (816±6) kJ/mol, (76.77±4) min^{-1} and (69.5±14) kJ/mol, (7.02±2) min^{-1}, respectively. The determination error in

the case of reduction by hydrogen does not exceed 7−10 %, whereas in the case of ammonia this value reaches 20 %;

5. The bulk density and specific surface area of final products obtained after reduction of uranium oxide samples do not change with respect to the initial values to be equal to 2.7−3.1 g/cm^3 and 0.3−0.4 m^2/g, respectively.

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