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Abstract

Full Text

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INTERACTION OF URANIUM TRIOXIDE WITH CRACKED AMMONIA IN THE PRESENCE OF ADDITIONS OF CERTAIN FOREIGN OXIDES

(Presented by Academician A. A. Balandin, 22 VIII 1963)

It is known that the presence of small amounts of foreign impurities during the reduction of metal oxides can sharply alter the course of the reduction process (^{1}). The starting UO_3 was prepared by decomposition of uranium peroxide (^{2}); it had a density of 6.5 g/cm^3 and a specific surface area of 15 m^2/g. The reducing agent was a nitrogen-hydrogen mixture ($3H_2 + N_2$), obtained by cracking ammonia over a nickel catalyst. The investigation was carried out in a high-vacuum circulation-type apparatus by the method of continuous weighing. The additions used were chemically pure-grade ZnO, TiO_2 with a content of foreign impurities of not more than 0.5%, and $UO_{2.04}$, obtained by reduction of chemically pure uranium sesquioxide–oxide. In all experiments, additions of oxides to UO_3 were introduced in an amount of 5 mol. %. The additions were introduced by careful grinding and mixing with the starting uranium trioxide. The pure UO_3 used in the control experiments was prepared in the same way. Before each experiment, weighed portions of the starting materials were dried in vacuum at 380°. The effect of temperature on the rate of reduction of pure UO_3 was studied in the range 350–500° at $P_{3H_2+N_2} = 200$ mm Hg (Fig. 1). Under analogous conditions, the effect of the ZnO addition was studied (Fig. 2). The remaining experiments were carried out at 400°. As is seen from Figs. 1-3, additions of ZnO and TiO_2 accelerated the reduction of uranium trioxide. The greatest increase in rate was caused by the ZnO addition. The presence of $UO_{2.04}$, however, somewhat slowed the process. Values of the apparent activation energies of the reduction process of UO_3 by cracked ammonia for different degrees of reduction are given in Table 1. They were determined from the Arrhenius equation by a graphical method.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 1. Reduction of UO_3 at various temperatures $P_{3H_2+N_2} = 200$ mm Hg (in %/min). 1—350°, 2—400°, 3—425°, 4—450°, 5—500°C

Table 1

Degree of reduction, %	6	19	45	85
Apparent activation energy, kcal/mol				
Without addition	26.5	28.7	35.6	31.7
Addition of 5 mol. % ZnO	35.8	35.1	35.4	33.1

Note. Complete conversion of UO_3 to UO_2 was taken as 100% reduction.

Every chemical reaction ultimately has an electronic mechanism. Of considerable interest are attempts to apply modern concepts of solid-state physics and the electron theory of adsorption and catalysis to the study of the mechanism of topochemical reactions (3–6). Although the cited works concern processes of thermal decomposition of various ionic compounds, S. Z. Roginskii believes (3) that a similar electronic mechanism is naturally to be expected also for reduction reactions of metal oxides and sulfides. The physical essence of this mechanism is that, all other conditions being equal, the rate of reduction of metal oxides will be governed by the concentration of free electrons on the surface of the oxide being reduced. From this point of view, it was of interest to investigate the influence of such additives which themselves do not interact chemically either with hydrogen or with uranium trioxide, but at the same time, possessing a definite type of conductivity, may affect the concentration of free electrons in the conduction band of the lattice of the oxide being reduced.

Fig. 2. Reduction of a mixture of UO_3+5 mol. % ZnO at various temperatures and $P_{3H_2+N_2} = 200$ mm Hg (in %/min).
1–350°, 2–375°, 3–400°, 4–425°, 5–450°, 6–475°, 7–500° C

Fig. 3. Reduction of UO_3 in the presence of additions of foreign oxides. $P_{3H_2+N_2} = 200$ mm Hg, $t = 400$°C (in %/min). Additives: 1–$UO_{2.04}$, 2–without additive, 3–TiO_2, 4–ZnO

ZnO and TiO_2 were chosen–semiconductors with electronic conductivity. Their reduction begins to proceed at an appreciable rate at 700 and 1050°, respectively. As a third additive, the oxide $UO_{2.04}$ was taken–a semiconductor with hole conductivity. In studying the electrical properties of uranium oxides (7), it was established that the oxides UO_3, U_3O_8, U_3O_7, and U_4O_9 are semiconductors with an excess of metal, i.e., of the n-type, whereas the oxide UO_{2+x}, where x varies from 0 to 0.13-0.16, is a semiconductor with a deficiency of metal, i.e., of the p-type. The electrical conductivities of systems whose total composition varies from $UO_{2.67}$ to $UO_{2.25}$ remain approximately constant throughout this entire range of compositions and are several orders of magnitude higher than the electrical conductivity of UO_3. Measurements carried out in our laboratory showed that at 200° the specific electrical conductivities of UO_3 and U_3O_8 are, respectively, $1 \cdot 10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ and $1 \cdot 10^{-2}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.

Guided by the principle of the sequence of chemical transformations of Acad. A. A. Baikov (8) and by the phase diagram of the uranium—oxy-

oxygen (9), one may expect the following scheme of phase transformations during the reduction of uranium trioxide:

$$UO_3 \rightarrow U_3O_8 \rightarrow U_3O_{8-x} \rightarrow U_4O_9 \rightarrow UO_{2+x} \rightarrow UO_2.$$

X-ray phase analysis of the reduction products was carried out by the powder method using copper K_α radiation in RKD cameras with a cassette diameter of 57.3 mm. The initial trioxide was X-ray amorphous. As the degree of reduction increased, lines of the crystalline structure of orthorhombic U_3O_8 appeared on the radiographs and became increasingly intense. Lines of other crystalline phases up to the composition $UO_{2.55}$ were not detected. Apparently, simultaneously with the reaction of reduction of UO_3 to U_3O_8, the sesquioxide is enriched with oxygen, which ends with the formation of the oxide $UO_{2.55}$, which is the lower limit of the solid solutions U_3O_{8-x}. Upon further removal of oxygen from U_3O_{8-x}, new lines of cubic structure appeared, while the intensity of the lines of the U_3O_{8-x} structure began to decrease. It should be noted that uranium oxides over the entire composition range from UO_2 to U_4O_9 possess a very similar crystalline structure, since the formation of the phases U_4O_9 and UO_{2+x} occurs through ordered (in the first case) and disordered (in the second) incorporation of oxygen into the face-centered cubic lattice of uranium dioxide. The oxides UO_2, UO_{2+x}, and U_4O_9 can be distinguished on radiographs only by the last lines at large reflection angles. The observed blurring of the cubic-structure lines at large reflection angles may indicate that reduction at this stage proceeded nonuniformly, i.e., mixtures of U_4O_9 and UO_{2+x} were formed. When the composition of the oxide phase reached $\sim UO_{2.25}$, the lines of uranium sesquioxide disappeared completely. Reduction ended with the formation of nonstoichiometric uranium dioxide UO_{2+x}. In radiographing samples containing additions of foreign oxides, no deviations from the picture described above were found. The formation of any chemical compounds of the main oxide with the oxide additives was not observed under the experimental conditions considered, even when the main oxide and the additive were taken in equimolar amounts.

In our studies, the process of reduction of UO_3 to U_3O_8 proceeded autocatalytically, which is associated with a change in the reaction surface. In our view, the following should additionally be borne in mind. The U_3O_8 arising during the reduction process is in close contact with the oxide being reduced. The electronic conductivity of uranium sesquioxide is several orders of magnitude higher than that of the trioxide. At the contact between them, a difference in the electrochemical potentials of the charge carriers arises. This leads to the transfer of some electrons from the U_3O_8 lattice into the UO_3 lattice. To check the correctness of this assumption, an additional experiment was carried out. A briquette was prepared consisting of two separate layers of trioxide and uranium sesquioxide, tightly pressed under a pressure of 2700 kg/cm^2, and the e.m.f. of the UO_3—U_3O_8 pair was measured. At 400° it proved to be equal to 53 mV. The sign of the e.m.f. corresponded to the transfer of electrons from U_3O_8 to UO_3. An increase in the concentration of free electrons in the conduction band of the oxide being reduced (UO_3) could lead to an increase in the rate of the crystallochemical transformation.

It was indicated above that the introduction of additions of ZnO and TiO_2 noticeably accelerated, while the presence of UO_{2+x} slowed, the reduction reaction of UO_3 to U_3O_8. At the same time, the presence of ZnO had practically no effect on the rate of reduction of $UO_{2.56}$ to $UO_{2.25}$. The apparent activation energy also did not depend on the presence of the ZnO additive. The following explanation of the observed facts appears possible. The oxides ZnO and TiO_2 are n-type semiconductors, and their electrical conductivity is considerably higher than that of uranium trioxide. In places of close contact between the oxide being reduced and the additive, there may ···

electron transfer can occur from the additive (ZnO or TiO_2) to UO_3, which leads to an increase in the rate of reduction of uranium trioxide. To test the validity of this assumption, we measured the e.m.f. of the UO_3—ZnO pair. At 400° it proved to be equal to 240 mV. On the other hand, the oxide $UO_{2.55}$ has sufficiently high electronic conductivity; therefore it is difficult to expect that the introduction of small amounts of n-type semiconductors will substantially affect the overall rate of its reduction. An admixture of the oxide $UO_{(2.04)}$, which has hole conductivity, can increase the probability of recombination of free electrons with positive holes. As a result, the concentration of free electrons decreases, and the reduction of UO_3 to U_3O_8 is slowed.

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