ISSN 1066-3622, Radiochemistry, 2008, Vol. 50, No. 1, pp. 46–51. © Pleiades Publishing, Inc., 2008.
Original Russian Text © M.Yu. Boltoeva, V.P. Shilov, A.V. Anan'ev, 2008, published in Radiokhimiya, 2008, Vol. 50, No. 1, pp. 41–46.

Catalytic Reduction of U(VI) with Formic Acid in Acid Solutions on Palladium Catalysts

M. Yu. Boltoeva, V. P. Shilov, and A. V. Anan'ev

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

Received November 30, 2006

Abstract—The kinetics of catalytic reduction of U(VI) with formic acid in H_2SO_4 solutions in the presence of Pd/SiO_2 catalysts differing in the size of nanocrystallites of the active metal was studied. A decrease in the size of supported Pd particles leads to a decrease in the specific activity of the catalyst, i.e., the catalytic centers located on large crystallites exhibit higher activity. An increase in the Pd percent content on SiO_2 leads to a decrease in the activity of the catalytic centers, which is caused by a considerable increase in the contribution of the side reaction of catalytic decomposition of HCOOH with an increase in the number of active centers in the catalyst grain. The results obtained are interpreted on the basis of the concepts of the energy nonuniformity of the surface atoms and of the reaction mechanism. The results show that the size of Pd nanocrystallites is an important factor of the selectivity of palladium catalysts in the preparation of U(IV) by catalytic reduction with formic acid.

PACS numbers: 82.20.Pm, 82.65.+r
DOI: 10.1134/S1066362208010062

Heterogeneous-catalytic processes can be successfully used for stabilization of the preset valence forms of actinides in process solutions of radiochemical plants.

One of important processes in the hydrometallurgy of the nuclear fuel cycle is the reduction of U(VI) to U(IV). One of the main chemical methods for preparing U(IV) is the reduction of U(VI) with hydrazine and HCOOH in the presence of platinum catalysts [1–6]. The major drawback of this method is the use of expensive platinum as the active component of the catalyst. In the course of natural wear and corrosion processes, platinum gets into radioactive waste fractions from which its recovery is impossible because of specific features of radiochemical technology. Therefore, search for and study of new catalysts for initiating redox reactions in aqueous media is an important scientific and practical problem.

One of promising materials for preparing the catalysts is Pd, which exhibits pronounced catalytic properties. In the previous paper [7] we showed that Pd/SiO_2 catalysts can be efficiently used for reducing U(VI) with hydrazine in moderately acidic nitrate-free solutions.

In this study we examined the kinetic relationships of the catalytic reduction of U(VI) with formic acid in acid solutions.

EXPERIMENTAL

Preparation and characterization of catalysts. Catalytic reduction of U(VI) was studied in the presence of various samples of Pd/SiO_2 catalysts differing in the percent content of Pd on the support and particle size of the active metal. We used the same catalyst samples as in [7]; their preparation and characterization procedures are described in [7]. The characteristics of the catalysts are given in Table 1. After each series of kinetic experiments, the catalysts were washed with water, dried at 100°C for 24 h, and then reused.

Experimental procedure. Kinetic experiments were performed in a temperature-controlled glass reactor equipped with a reflux condenser to prevent evaporation of the working solutions. In addition, the

Table 1. Characteristics of Pd/SiO_2 catalysts

Catalyst	Actual Pd content, %	Mean particle diameter d_{vs}, nm	Dispersity $D_{Pd} = 1.12/d_{vs}$
1% Pd/SiO_2 (A)	0.89	12.9	0.086
1% Pd/SiO_2 (B)	0.76	8.8	0.130
4% Pd/SiO_2 (A)	3.92	12.7	0.088
4% Pd/SiO_2 (B)	4.1	12.3	0.091

reaction vessel was protected from light to eliminate possible contribution of photochemical processes. The working solutions were prepared just before the experiment by mixing the calculated amounts of solutions of H_2SO_4, HCOOH, uranyl sulfate, and distilled water. The total volume of the reaction mixture was 20 ml. After thermostating at a required temperature, the catalytic reduction of U(VI) was initiated by introducing a weighed portion of a dry catalyst into the reactor. The mixture was agitated by argon bubbling at a definite rate monitored with a float-type flow meter. To determine the current concentrations of U(IV), we took at regular intervals 0.2-ml aliquots of the working solution, mixed them with 2 ml of 2.0 M H_2SO_4, and measured the optical density at λ = 650 nm. The spectra were recorded with a Shimadzu 3100 spectrophotometer.

The hydrogen content of gaseous reaction products was determined with a Chrom 5 chromatograph (column length 2 m, column packed with 5A molecular sieves, granule size 0.4–0.5 mm, thermal conductivity detector, carrier gas Ar, flow rate 30 ml min^{-1}, room temperature).

RESULTS AND DISCUSSION

Preliminary experiments showed that palladium catalysts do not initiate the reduction of U(VI) with formic acid in nitric acid solutions in a wide range of experimental conditions, even after adding hydrazine as antinitrite agent. In sulfuric acid, HCOOH starts to reduce U(VI) in the presence of 0.1 g ml^{-1} of 1% Pd/SiO_2 at a noticeable rate even at 30°C. At 60°C, a 0.05 M solution of U(VI) in 0.5 M H_2SO_4 is completely reduced with 0.5 M HCOOH within 1 h.

To determine the order of the catalytic reaction with respect to the U(VI) concentration, we performed a series of experiments in the range of initial U(VI) concentrations from 0.02 to 0.2 M (Fig. 1a). Analysis of the dependence of the initial reaction rate on the initial U(VI) concentration (Fig. 1b) shows that the reduction of U(VI) follows a first-order law with respect to [U(VI)]. Therefore, we calculated the first-order rate constants k_1 by the equation $-dC/d\tau = k_1C$.

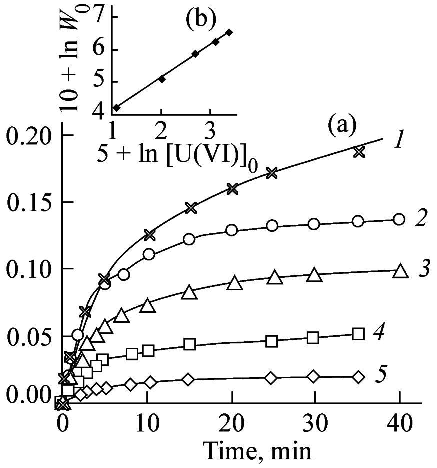

Fig. 1. (a) Kinetic curves of U(VI) reduction at its different initial concentrations $[U(VI)]_0$ and (b) initial reaction rate as a function of $[U(VI)]_0$. Reaction system: 0.5 M H_2SO_4, 0.5 M HCOOH, 0.05 g ml^{-1} of 1% Pd/SiO_2 (A); 60°C. (a) $[U(VI)]_0$, M (*1*) 0.2, (*2*) 0.15, (*3*) 0.1, (*4*) 0.05, and (*5*) 0.02; (b) n = 1.022, R^2 = 0.999.

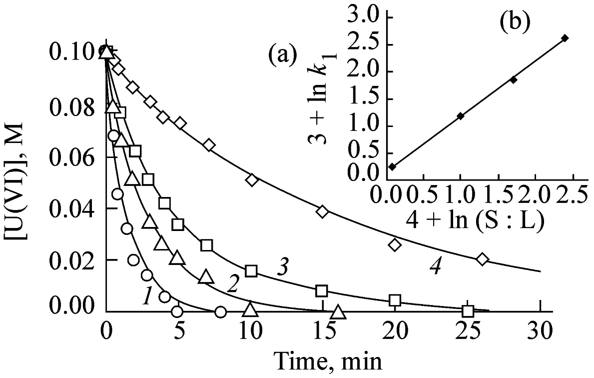

Fig. 2. (a) Kinetic curves of reduction of 0.1 M U(VI) in the presence of various amounts of 1% $PdSiO_2$ (A) and (b) influence of the S : L ratio on the rate of catalytic reduction of U(VI) at $[H_2SO_4]$ = 0.5, [HCOOH] = 0.5 M; 60°C. (a) Amount of 1% Pd/SiO_2 (A), g ml^{-1}: (*1*) 0.2, (*2*) 0.1, (*3*) 0.05, and (*4*) 0.02; (b) n = 1.03, R^2 = 0.9992.

The kinetic curves of the catalytic reduction of 0.1 M U(VI) in 0.5 M H_2SO_4 in the presence of 0.5 M HCOOH and various amounts (S : L ratios) of 1% Pd/SiO_2 (A) at 60°C are shown in Fig. 2a. An increase in the catalyst amount from 0.02 to 0.2 g ml^{-1} leads to a proportional increase in the rate of U(VI) reduction, which is typical of heterogeneous-catalytic processes. In the coordinates $\ln[S:L]–\ln k_1$, this dependence is a straight line with a slope of 1.03 (Fig. 2b), which can be formally interpreted as the apparent reaction order with respect to the volumetric concentration of active catalytic centers in the reaction system.

The values of k_1 for various catalysts and experimental conditions are given in Table 2. The calculations, as a rule, were based on the results of three independent kinetic experiments. The error in the determination of k_1 did not exceed ~10%, which is typical of kinetic measurements.

Table 2. Catalytic reduction of U(VI) with formic acid in sulfuric acid solutions in the presence of palladium catalysts

$[U(VI)]_0$, M	S : L, g ml^{-1}	[HCOOH], M	$[H_2SO_4]$, M	T, °C	k_1, min^{-1}
1% Pd/SiO_2 (A)					
0.1	0.02	0.5	0.5	60	6.36×10^{-2}
0.1	0.05	0.5	0.5	60	1.61×10^{-1}
0.1	0.1	0.5	0.5	60	3.16×10^{-1}
0.1	0.2	0.5	0.5	60	6.88×10^{-1}
0.02	0.05	0.5	0.5	60	1.49×10^{-1}
0.05	0.05	0.5	0.5	60	1.52×10^{-1}
0.1	0.05	0.5	0.5	60	1.58×10^{-1}
0.15	0.05	0.5	0.5	60	1.52×10^{-1}
0.2	0.05	0.5	0.5	60	1.43×10^{-1}
0.05	0.05	0.1	0.5	60	1.17×10^{-1}
0.05	0.05	0.2	0.5	60	1.28×10^{-1}
0.05	0.05	0.3	0.5	60	1.98×10^{-1}
0.05	0.05	0.5	0.5	60	1.65×10^{-1}
0.05	0.05	1	0.5	60	1.36×10^{-1}
0.05	0.05	2	0.5	60	1.68×10^{-1}
0.05	0.05	3	0.5	60	1.78×10^{-1}
0.05	0.05	0.5	0.3	60	1.46×10^{-1}
0.05	0.05	0.5	0.5	60	1.56×10^{-1}
0.05	0.05	0.5	1	60	1.58×10^{-1}
0.05	0.05	0.5	2	60	1.42×10^{-1}
0.05	0.05	0.5	3	60	1.52×10^{-1}
0.05	0.05	0.5	0.5	30	3.60×10^{-2}
0.05	0.05	0.5	0.5	40	6.41×10^{-2}
0.05	0.05	0.5	0.5	50	1.12×10^{-1}
0.05	0.05	0.5	0.5	60	1.52×10^{-1}
0.05	0.05	0.5	0.5	70	2.86×10^{-1}
1% Pd/SiO_2 (B)					
0.05	0.05	0.5	0.5	30	4.17×10^{-2}
0.05	0.05	0.5	0.5	40	6.79×10^{-2}
0.05	0.05	0.5	0.5	50	9.25×10^{-2}
0.05	0.05	0.5	0.5	60	1.24×10^{-1}
0.05	0.05	0.5	0.5	70	1.83×10^{-1}
4% Pd/SiO_2 (A)					
0.05	0.05	0.5	0.5	32	5.34×10^{-2}
0.05	0.05	0.5	0.5	40	7.13×10^{-2}
0.05	0.05	0.5	0.5	50	1.22×10^{-2}
0.05	0.05	0.5	0.5	60	1.52×10^{-1}
0.05	0.05	0.5	0.5	70	2.14×10^{-1}
4% Pd/SiO_2 (B)					
0.05	0.05	0.5	0.5	32	6.32×10^{-2}
0.05	0.05	0.5	0.5	40	8.48×10^{-2}
0.05	0.05	0.5	0.5	50	1.04×10^{-1}
0.05	0.05	0.5	0.5	60	1.48×10^{-1}
0.05	0.05	0.5	0.5	70	1.8×10^{-1}

The main kinetic relationships of the catalytic reduction of U(VI) with formic acid in sulfuric acid solutions were studied in the presence of 1% Pd/SiO_2 (A). The dependence of the rate constant of U(VI) reduction on the HCOOH concentration in the range 0.1–3 M is complex. The reaction rate first increases with an increase in [HCOOH] from 0.1 to 0.3 M, after which it somewhat decreases and the remains virtually constant in the range of [HCOOH] 1.0–3.0 M (Fig. 3).

An increase in the H_2SO_4 concentration in the range 0.1–3 M at $[U(VI)]_0 = 0.05$, [HCOOH] = 0.5 M and 60°C in the presence of 0.1 g ml^{-1} of 1% Pd/SiO_2 (A) does not lead to a noticeable change in k_1. This fact indicates that hydrogen ions do not directly participate in the rate-determining step of the reaction.

Table 2 shows that all the catalysts exhibit similar catalytic activity (per unit weight of the catalyst) in the reduction of U(VI). Unexpectedly, the catalyst activity does not increase with a fourfold increase in the Pd content on the support.

The specific activity of the catalysts was evaluated by the turnover number r (min^{-1}), i.e., by the number of catalytic events per surface atom of the catalyst in unit time. The quantity r was calculated by the formula $r = \omega V/N$, where ω is the reaction rate in the mol l^{-1} min^{-1} units; V, volume of the reaction mixture in liters; and N, number of moles of surface Pd atoms. The number of surface atoms of the catalyst, involved in the heterogeneous-catalytic process, was calculated from the catalyst weight, percent content of Pd on the support, and metal dispersity determined by electron microscopy. Because the rate of U(VI) reduction [first order with respect to $[UO_2^{2+}]$) decreases with the reaction progress, as parameter ω we took the change in the HCOOH concentration within the half-conversion time $\tau_{1/2} = \ln 2/k_1$ (k_1 is the first-order rate constant), normalized with respect to $\tau_{1/2}$, i.e., we took $\omega = C_0/2\tau_{1/2}$ [C_0 is the initial concentration of U(VI)]. The turnover numbers calculated for $[U(VI)]_0 = 0.05$, [HCOOH] = 0.5, $[H_2SO_4] = 0.5$ M and $T = 60$°C with various catalysts are given in Table 3. As can be seen, the specific (per surface atom) activity of palladium catalysts depends not only on the size of nanoaggregates of the active metal, but also on the percent content of the metal on the support, i.e., surface Pd atoms located on coarse crystallites exhibit higher catalytic activity. At the same time, an increase in the percent content of Pd on SiO_2 decreases the activity of the catalytic centers.

The temperature dependences of the rates of catalytic reduction of U(VI) with HCOOH in sulfuric acid solutions were measured in the presence of various palladium catalysts. In the Arrhenius coordinates, these dependences are straight lines in the temperature range 30–70°C. The corresponding apparent activation energies are given in Table 4. With the catalyst 4% Pd/SiO_2 in the temperature range 30–50°C, an induction period (about 6 min) is observed. Our results show that, under equal other conditions, the apparent activation energy depends on the size of Pd particles and metal content on the support.

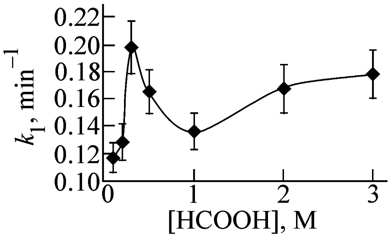

Fig. 3. Rate of catalytic reduction of U(VI) as a function of HCOOH concentration at $[U(VI)]_0 = 0.05$, $[H_2SO_4] = 0.5$ M and 60°C in the presence of 0.05 g ml^{-1} of 1% Pd/SiO_2 (A).

An important property of HCOOH is the capability for catalytic decomposition to H_2 and CO_2 in the presence of Pd metal. The kinetics and mechanism of this reaction in aqueous solutions have been described in detail in [8]. Therefore, to understand the mechanisms of catalytic reactions in the system U(VI)–HCOOH–Pd/SiO_2, it is very important to examine whether the reduction of U(VI) and catalytic dehydrogenation of HCOOH occur concurrently. To detect possible formation of H_2 in the course of catalytic reduction of U(VI) with formic acid, we performed a chromatographic analysis of the gaseous reaction products for the H_2 content. Figure 4 shows how the

Table 3. Influence of the size of Pd nanoaggregates on the specific activity of Pd/SiO_2 catalysts in the reduction of U(VI) with formic acid in sulfuric acid solutions at $[U(VI)]_0 = 0.05$, [HCOOH] = 0.5, $[H_2SO_4] = 0.5$ M and $T = 60$°C

Catalyst	d_{vs}, nm	D	r, min^{-1}
1% Pd/SiO_2 (A)	12.9	0.086	14.96
1% Pd/SiO_2 (B)	8.8	0.130	7.33
4% Pd/SiO_2 (A)	12.7	0.088	2.65
4% Pd/SiO_2 (B)	12.3	0.091	2.50

Table 4. Apparent activation energies of the reduction of U(VI) with formic acid in sulfuric acid solutions in the presence of various palladium catalysts at $[U(VI)]_0 = 0.05$, [HCOOH] = 0.5, $[H_2SO_4] = 0.5$ M and S : L = 0.05 g ml^{-1}

Catalyst	d_{vs}, nm	E^*, kJ mol^{-1}
1% Pd/SiO_2 (A)	12.9	43.3 ± 3.5
1% Pd/SiO_2 (B)	8.8	30.8 ± 1.5
4% Pd/SiO_2 (A)	12.7	32.0 ± 2.3
4% Pd/SiO_2 (B)	12.3	24.0 ± 1.0

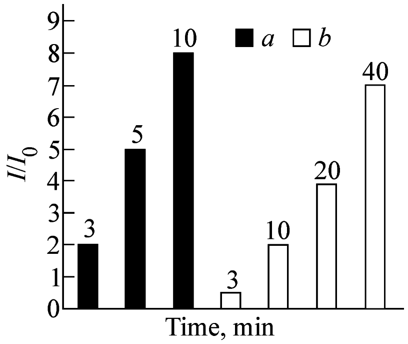

Fig. 4. Variation of the intensity of the chromatographic peak of H_2 with time in the course of (*a*) catalytic decomposition of HCOOH and (*b*) catalytic reduction of U(VI) ($[U(VI)]_0$ = 0.05 M) with formic acid ([HCOOH] = 0.3, $[H_2SO_4]$ = 0.5 M) on the catalyst 4% Pd/SiO_2 (A) at 60°C.

intensity of the chromatographic peak of H_2 varies with time in the course of catalytic decomposition of HCOOH and catalytic reduction of U(VI) with formic acid on the catalyst 4% Pd/SiO_2 (A) at 60°C. These data show that both reactions are accompanied by the evolution of gaseous H_2. Since H_2 cannot be formed in the oxidation of HCOOH with U(VI), we can conclude that the evolution of H_2 in the course of catalytic reduction of U(VI) with formic acid on a Pd/SiO_2 catalyst is due to the side reaction of the catalytic decomposition of HCOOH in the presence of Pd, occuring concurrently with the main process.

The results we obtained allow certain assumptions concerning the mechanism of catalytic reduction of U(VI) with HCOOH in sulfuric acid solutions in the presence of a palladium catalyst. Most probably, as in the case of catalytic decomposition of HCOOH on Pd [8], the reaction starts with reversible chemisorption of HCOOH molecules on the catalyst surface, with two adjacent catalytic centers participating in the process:

$$2Pd + HCOOH \rightleftarrows Pd(H) + Pd(HCOO). \quad (1)$$

Ruthven and Upadhye [8] soundly believe that the chemisorbed formate radical undergoes an intramolecular transformation to form a chemisorbed H atom and a free CO_2 molecule:

$$Pd(HCOO) \rightarrow Pd(H) + CO_2. \quad (2)$$

The H atoms bonded to catalytic centers can reduce uranyl ions in a one-electron process:

$$Pd(H) + UO_2^{2+} \rightarrow UO_2^{+} + H^+ + Pd, \quad (3)$$

which is apparently the rate-determining step of the reaction, or reversibly recombine with the evolution of molecular hydrogen:

$$Pd(H) + Pd(H) \rightleftarrows H_2 + 2Pd, \quad (4)$$

with the rates of reactions (3) and (4) being comparable, as follows from the accumulation of H_2 in gaseous reaction products.

Uranium(V) formed by reaction (3) rapidly disproportionates into U(VI) and U(IV):

$$2UO_2^{+} + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O. \quad (5)$$

The above sequence of reactions (1)–(5) describes the catalytic reduction of U(VI) under the assumption that the chemisorbed formate radical, which exhibits pronounced reductive properties, decomposes by reaction (2) faster than effects one-electron reduction of uranyl ion. Otherwise, the fast radical reaction

$$UO_2^{2+} + Pd(HCOO) \rightarrow UO_2^{+} + H^+ + CO_2 + Pd \quad (6)$$

would be possible. In this case, reaction (3) will also be the slow, rate-determining step of the process, because of the pronounced tendency of Pd to form fairly stable compounds with H_2 [9] and, hence, of the decreased reactivity of the chemisorbed hydrogen atom compared to the COOH radical.

The above reaction pathways are kinetically indiscernible. Summation of the reaction equations for both schemes, taking into account the stoichiometric coefficients, yields to the same overall reaction equation:

$$UO_2^{2+} + HCOOH + 2H^+ = U^{4+} + CO_2 + 2H_2O, \quad (7)$$

and therefore it is impossible to choose one of the two reaction pathways on the basis of the available experimental data.

The above-presented possible pathways of the reduction of U(VI) with formic acid in the presence of Pd/SiO_2 are reasonably consistent with the kinetic parameters of the process. The first reaction order with respect to [U(VI)] and the independence of the reaction rate from the concentration of H^+ ions directly follow from the suggested reaction mechanisms. The complex dependence of the reduction rate on [HCOOH] may be due to changes in the relative contributions of concurrent reactions (3) and (4) to the overall catalytic process with an increase in the coverage of the active surface of the catalyst as [HCOOH] is increased. However, the origin of the statistically significant maximum in the curve of the rate of U(VI) reduction vs. [HCOOH] (Fig. 3) is unclear.

The dependence of the catalytic activity of surface Pd atoms on the size of metal nanoaggregates (Table 3) indicates that the catalytic reduction of U(VI) with formic acid in sulfuric acid solutions is a structure-sensitive process. The negative size effect is observed. These results are also rationalized on the basis of the suggested reaction mechanism. Indeed, a decrease in the nanoaggregate size should lead to an increase in the relative content of apical and edge coordination-unsaturated atoms [10]. It is reasonable to expect that the energy of the chemical bond of hydrogen atoms with such low-coordinate surface Pd atoms will be higher than with atoms located on crystallite faces. As the ease of oxidation of such species with uranyl ion will be determined by the Pd–H bond energy, its increase will make the oxidation more difficult and hence decrease the specific activity of the catalyst.

The unexpected, at first glance, lack of noticeable increase in the activity of palladium catalysts in the reduction of U(VI) with formic acid at a fourfold increase in the content of the active metal on the support is also quite explicable. Actually, the point is that the specific activity of the catalyst considerably decreases with an increase in the Pd content (Table 3). This trend is apparently caused by a considerable increase in the contribution of the side reaction, catalytic decomposition of HCOOH, with an increase in the number of active centers in the catalyst grain, at constant concentrations of U(VI) and HCOOH in the reaction system. Indeed, the chemisorbed hydrogen atom Pd(H) is a common active participant of the reduction of U(VI) and decomposition of HCOOH on Pd, and the rates of the main (3) and side (4) reactions will be proportional to [U(VI)][Pd(H)] and $[\mathrm{Pd(H)}]^2$, respectively. Since at equal HCOOH concentrations the number of the formed active species Pd(H) in each catalyst grain will increase in proportion to the number of catalytic centers, an increase in the Pd content on the support will apparently accelerate the decomposition of HCOOH to a considerably greater extent than the reduction of U(VI). Notably, in the reduction of U(VI) with hydrazine on $\mathrm{Pd/SiO_2}$ catalysts [7], where the main process is not accompanied by the side reaction of catalytic decomposition of N_2H_4, this trend is not observed.

When a catalytic process is accompanied by side reactions, the selectivity of catalytic materials becomes an important factor. One of important requirements to a catalyst is its selectivity with respect to the target process, i.e., the side reactions should be reduced to a minimum with the high catalytic activity in the main process preserved. In the catalytic reduction of U(VI) with formic acid in the presence of palladium catalysts, the decomposition of HCOOH is such a side reaction. As follows from [8], the catalytic decomposition of HCOOH on Pd is a structure-independent process. At the same time, as we showed, the specific activity of the catalyst in the reduction of U(VI) increases with an increase in the size of Pd nanocrystallites on the support (negative size effect). Thus, an increase in the size of Pd particles on the support favors a decrease in the contribution of the side reaction of HCOOH decomposition and hence an increase in the relative yield of U(IV). Thus, the dispersity of the active component in $\mathrm{Pd/SiO_2}$ is an important selectivity factor in the catalytic reduction of U(VI) with formic acid. Therefore, when preparing U(IV) by catalytic reduction with formic acid, the use of coarsely dispersed palladium catalysts is preferable.

REFERENCES

1. Swanson, J.L., Platinum Catalyzed Hydrazine Reduction of Plutonium(IV) and Uranium(VI), *BNWL-1584*, 1971.
2. Zanelli, S., *Ingegneria Nucl.*, 1967, vol. 8, p. 23.
3. Delange, M., Chambon, M., and Patigny, M., *Energ. Nucl.* (France), 1971, vol. 13, p. 94.
4. Abdunnabi, H.M. and Ananiev, A.V., in *Proc. Int. Conf. on Fast Reactors and Related Nuclear Fuel Cycles*, Kyoto (Japan), 1991, vol. IV, pp. 6.9–6.16.
5. Abdunnabi, H.M., Ananiev, A.V., and Krot, N.N., *J. Radioanal. Nucl. Chem., Lett.*, 1994, vol. 186, pp. 89–97.
6. Anan'ev, A.V., Shilov, V.P., Afonas'eva, T.V., et al., *Radiokhimiya*, 2001, vol. 43, no. 1, pp. 37–40.
7. Boltoeva, M.Yu., Trefilova, A.V., Shilov, V.P., and Anan'ev, A.V., *Radiokhimiya*, 2008, vol. 50, no. 1, pp. 34–40.
8. Ruthven, D.M. and Upadhye, R.S., *J. Catal.*, 1971, vol. 21, pp. 39–47.
9. Lewis, F.H., *The Palladium–Hydrogen System*, New York: Academic, 1967.
10. Bukhtiyarov, V.I. and Slin'ko, M.G., *Usp. Khim.*, 2001, vol. 70, no. 2, pp. 168–181.