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

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Abstract—The stability of finely dispersed palladium supported on silica gel with respect to various acids was studied. It was shown that palladium catalysts can be used in moderately acidic media under reducing conditions. In nitric acid solutions within a wide range of experimental conditions, the palladium catalysts do not initiate reduction of U(VI) with hydrazine. The catalytic properties of palladium catalysts differing in the size of nanocrystallites of the active metal were examined in the reduction of U(VI) with hydrazine in sulfuric acid solutions. The specific activity of Pd/SiO₂ catalysts is determined solely by the size of metal nanocrystals and is independent of the metal content on the support. The negative size effect is observed, i.e., the surface Pd atoms located on large crystallites exhibit higher catalytic activity. The results obtained were interpreted on the basis of the concepts of the energy nonuniformity of the surface atoms and of the mechanism of U(VI) catalytic reduction with hydrazine in the sulfuric acid solutions.

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Preparation of U, Np, and Pu in the preset oxidation states and many stages of nuclear fuel reprocessing and radioactive waste treatment are sometimes complicated by low rate of the redox reactions. They can be accelerated by heterogeneous catalysts based on platinum-group metals.

The set of catalytic materials used is mainly restricted to finely dispersed Pt on inert supports [1]. It should be noted that, in spite of the efficiency and evident advantages of the catalytic processes, they have not found universal use in the existing radiochemical technologies. The major factor limiting their use is probably high cost of platinum required for production of the catalysts. Therefore, search of platinum substitutes exhibiting catalytic activity in redox processes in solutions is an urgent problem.

Palladium is one of such promising materials. As a platinoid, palladium is characterized by pronounced catalytic properties. In addition, Pd is one of the uranium fission products and is accumulated in nuclear waste. The methods of its concentration and recovery from radioactive solutions are well known and developed [2–4]. Therefore Pd, in principle, can be repeatedly used within the framework of a nuclear fuel cycle. The expected disadvantage of Pd is the lower chemical stability as compared to Pt.

In this study, we examined the stability of silicasupported finely dispersed palladium with respect to various acids to determine the limits of application of palladium catalysts and evaluated the catalytic properties of Pd in the reduction of U(VI) into U(IV) with hydrazine.

EXPERIMENTAL

Preparation and characterization of catalysts. Catalysts containing 1 and 4% Pd/SiO₂, differing in the dispersity of the active metal, were prepared by impregnation of MSK silica gel grains (granule size 0.8-1.0 mm) with a solution of PdCl₂ in 2 M HCl. The volume ratio of the support to the precursor solution was about 1 : 1.2. The mixture was dried initially in a desiccator over NaOH to obtain a friable, slightly wet product and then in an oven at $100-110^{\circ}$ C to the air-dry state. The support with the precursor applied was divided in two portions. The first of them was calcined in air at 350°C for 2 h and then reduced with hydrogen at 400°C for 2 h (method A). The second portion was reduced with hydrogen at 400°C for 2 h without preliminary calcination in air (method B).

The Pd content on silica gel was determined spectrophotometrically using a color reaction with $SnCl_2$ after washing out Pd from the catalyst sample with aqua regia [5]. The average size of Pd crystallites (coherent scattering regions) on SiO₂ was determined from the broadening of the (111) X-ray diffraction

Catalyst	Actual Pd content, %	$d_{\rm diffr} = \lambda/\beta \cos \theta$, nm	$d_{\rm vs} = \sum n_i d_i^3 / \sum n_i d_i^2$, nm	$D_{\rm Pd} = 1.12/d_{\rm vs}$
1% Pd/SiO ₂ (A)	0.89	11.5	12.9	0.086
$1\% \text{ Pd/SiO}_2(B)$	0.76	_*	8.8	0.130
$4\% \text{ Pd/SiO}_2(A)$	3.92	11.0	12.7	0.088
$4\% \text{ Pd/SiO}_2(B)$	4.1	10.6	12.3	0.091

Table 1. Characteristics of Pd/SiO₂ catalysts

* X-ray amorphous material.

line. The line profiles were recorded on an ADP-10 Philips diffractometer (Cu K_{α} radiation, graphite monochromator, diffracted beam) and approximated by the Gaussian curve. The instrumental linewidth was determined by nonlinear interpolation of the linewidth of the Si powder. Broadening of the (111) line was determined by the formula $\beta = (B^2 - b^2)^{1/2}$, where B is observed and b, instrumental linewidth. The crystallite size (in nanometers) was determined by the formula $d = \lambda/\beta \cos \theta$ [6], where β is expressed in radians (2θ units). The electron microanalysis of the catalysts synthesized was performed on a Philips EM-301 transmission electron microscope. The size distribution of the metal particles was estimated by measuring and counting a large number of crystallites. The average surface-volumetric size of crystallites was determined by the formula $d_{vs} = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of crystallites with diameter d_i [7]. The dispersity of the active component (the ratio of the number of the surface metal atoms to the total number of metal atoms on the support) was determined from the equation $D_{\rm M} = (6/d)(v_{\rm M}/a_{\rm M})$ [8], where $a_{\rm M}$ is the average effective area occupied by the metal on the surface and $v_{\rm M}$, atomic volume of the metal phase. For Pd, $D_{Pd} = 1.12/d$.

Experimental procedure. The kinetic experiments were performed in a temperature-controlled glass reactor equipped with a reflux condenser to prevent evaporation of working solutions. Working solutions were prepared just before the experiment by mixing the calculated amounts of H2SO4, N2H4, uranyl sulfate, and distilled water. The total volume was 20 ml. After thermostatic control of a mixture 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 reaction mixture was agitated by argon bubbling at a constant rate. The agitation intensity was controlled by a float-type flow meter. 0.2-ml aliquots of the working solutions were taken for analysis at regular intervals. The current U(IV)concentration in the solution was monitored spectrophotometrically at 650 nm. The epectra were recorded on a Shimadzu 3100 spectrophotometer.

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The stoichiometry of the catalytic reduction of U(VI) was determined after keeping the reaction mixture with the catalyst in the reactor at a required temperature until the reaction completion. Then the solution was separated from the catalyst by filtration, combined with wash waters, and transferred into a volumetric flask. A sample for analysis was diluted by a factor of 3 with water, and NaOH was added to precipitate uranium hydroxide. The precipitate was separated by centrifugation, and the solution with wash water was transferred into a titration flask. The hydrazine concentration in the solution was determined by iodometric titration in NH₄HCO₃ solution.

RESULTS AND DISCUSSION

The results of the chemical analysis of the catalysts synthesized, size of Pd crystallites determined by different methods, and dispersity characteristics of the active component are listed in Table 1. The catalyst 1% Pd/SiO₂ (B) appeared to be X-ray amorphous, which did not allow calculation of the average crystallite size of the active component from broadening of the X-ray diffraction lines. Therefore, to compare the dispersity of all catalysts, we used the average surface-volumetric size of nanoaggregates d_{vs} , found from the data of electron microscopy.

The loss of Pd from the catalyst due to dissolution in mineral acid solutions was measured for the catalyst 1% Pd/SiO₂ (B) at room temperature and S : L = 0.1 g ml⁻¹ (Table 2). The data obtained showed that silica-supported finely dispersed Pd is unstable in sulfuric and nitric acid solutions. In sulfuric acid, Pd passes into the solution due to oxidation of the surface of the finely dispersed metal particles with atmospheric oxygen and dissolution of the oxide formed in the acid. The observed sharp decrease in the Pd loss in the H₂SO₄ solutions deaerated by argon bubbling confirms this assumption. The Pd dissolution in nitric acid solutions decelerates in the presence of antinitrite agents (urea). The presence in the acid solutions of a reductant, hydrazine, sharply enhances the stability

Table 2. Influence of solution composition on Pd loss from 1% Pd/SiO₂ (B) catalyst at room temperature (S : L = 0.1 g ml⁻¹; contact time 7 days)

Solution composition, M	Pd loss, %
1.0 H ₂ SO ₄	23.9
$2.0 \text{ H}_2\text{SO}_4$	34.5
$3.0 \text{ H}_2 \text{SO}_4$	41.0
$1.0 \text{ H}_2 \text{SO}_4^*$	5.2
0.5 HNO ₃	16.6
0.7 HNO ₃	20.4
1.0 HNO ₃	28.2
1.5 HNO ₃	100
$1.0 \text{ HNO}_{3} + 0.1 \text{ CO}(\text{NH}_{2})_{2}$	12.1
$1.5 \text{ HNO}_3 + 0.1 \text{ CO}(\text{NH}_2)_2$	17.3
$0.5 H_2 SO_4 + 0.2 N_2 H_4 * * 2$	0
$0.5 \text{ HNO}_{3} + 0.2 \text{ N}_{2} \text{H}_{4}^{+**}$	2.8

* Argon bubbling.

of the catalyst. A minor Pd dissolution in the nitric acid solution in the course of contact for a week is probably associated with catalytic decomposition of hydrazine. It was shown in a special experiment that, during 6-h agitation with argon at 70°C of 1 M HNO₃ or 2 M H₂SO₄ containing 0.2 M hydrazine and 0.1 g ml⁻¹ of 1% Pd/SiO₂ (B), Pd did not pass into the solution, i.e., the palladium catalysts can be successfully used in moderately acidic media under the reducing conditions.

Preliminary experiments showed that palladium catalysts did not initiate U(VI) reduction with hydrazine in nitric acid solutions in a wide range of the experimental conditions. Introduction of 0.1 g ml⁻¹ of 1–4% Pd/SiO₂ into 0.05–1.0 M U(VI) solutions in 0.5–2.0 M HNO₃ containing 0.1–1.0 M N₂H₄ at 50–70°C causes decomposition of hydrazine, but U(IV) is not formed. In sulfuric acid, hydrazine reduces U(VI)



Fig. 1. Kinetic curves of reduction of 0.05 M U(VI) in 0.5 M H_2SO_4 in the presence of 0.2 M N_2H_4 and various amounts of 1% Pd/SiO₂ (A) at 60°C. Catalyst amount, mg l⁻¹: (1) 0.2, (2) 0.1, (3) 0.05, and (4) 0.02.

in the presence of 0.1 g ml⁻¹ of 1% Pd/SiO₂ at a noticeable rate even at 30°C. At 60°C, 0.1 M U(VI) in 0.5 M H_2SO_4 is completely reduced in the presence of 0.2 M N_2H_4 within less than 2 h.

To determine the stoichiometry of the process, we performed a series of experiments in which the N₂H₄ consumption was determined under various conditions. It was found that, within the 40–70°C temperature range, the stoichiometric coefficient $n = \Delta[N_2H_5^+/\Delta[U(IV)]]$ remained constant and equal to 0.4–0.5, irrespective of whether a fresh or aged catalyst was used. This fact suggests that, in the entire range of the experimental conditions, the catalytic reduction of U(VI) with hydrazine is described by the stoichiometric equation

$$2UO_2SO_4 + N_2H_5HSO_4 + H_2SO_4 = 2U(SO_4)_2 + N_2 + 4H_2O.$$
 (1)

After the completion of U(VI) reduction, the N_2H_4 concentration did not change for a long time, which indicates that palladium catalysts do not promote decomposition of hydrazine in sulfuric acid solution.

The kinetic curves of the catalytic reduction of 0.05 M U(VI) in 0.5 M H₂SO₄ in the presence of 0.2 M hydrazine and various amounts of 1% Pd/SiO₂ (S:L ratio) at 60°C are shown in Fig. 1. The characteristic feature of the process is the fact that the introduction of the catalyst into the working solution initially causes rapid reduction of uranium in an amount approximately proportional to catalyst amount, after which the reduction decelerates. Such a shape of the kinetic curves suggests the occurrence of two successive processes. The first, fast reaction is probably stoichiometric rather than catalytic. It is caused by fast conditioning of the catalyst surface upon its contact with the reaction medium. The second, slower stage is a result of the steady-state catalyst action. In a separate series of experiments, we showed that the mode of launching the reaction (order of adding reactants) does not affect the shape of the kinetic curve and rate of U(VI) reduction.

The fast formation of U(IV) in the initial step of the reaction of the dissolved components with the catalyst surface suggests that this process is a consequence of the radical reaction of uranyl ions with active reducing species arising during reaction of the surface Pd atoms with hydrazine. Taking into account the tendency of Pd to form hydride-type compounds with hydrogen [9], we can suggest the formation in the reaction mixture of radicals $N_2H_3^2$

^{**} Residual hydrazine concentration 0.2 (with H₂SO₄) and 0.03 M (with HNO₃)

generated in the reaction

$$Pd + N_2H_4 \rightarrow Pd(H) + N_2H_3^{\bullet}, \qquad (2)$$

followed by their reaction with uranyl ions:

$$UO_2^{2+} + N_2H_3^{\bullet} \rightarrow UO_2^{+} + H_2N-N^{\bullet} + H^+.$$
 (3)

The kinetics of such reaction can be described by the equation

$$-d[UO_2^{2^+}]/d\tau = k'[UO_2^{2^+}][N_2H_3^{\bullet}].$$
(4)

Since the amount of $N_2H_3^{*}$ radicals generated during the initial conditioning of the catalyst surface is equal to the number of the surface Pd atoms in the reaction system, Eq. (4) can be written as follows:

$$-dC/d\tau = k'C[(A - C_0) + C], \qquad (5)$$

where k', $1 \text{ mol}^{-1} \text{ min}^{-1}$, is a rate constant of the bimolecular reaction, and C and C_0 , current and initial U(VI) concentrations, respectively. The constant A is equal to MD(S : L)/106.4, where M is a Pd weight fraction on the support; D, catalyst dispersity; S : L, ratio of the catalyst weight to solution volume; and 106.4, Pd atomic weight.

The mathematical treatment of the initial portions of the kinetic curves and calculation of k' were performed with the Table Curve 2D (Jandel Scientific) software.

To determine the order of the slow catalytic reaction with respect to the U(VI) concentration, we carried out a series of experiments within the [U(VI)] range from 0.01 to 0.2 M. The analysis of the kinetic curves (Fig. 2) shows that the reaction order with respect to [U(VI)] decreases from 1 to 0 with an increase in the U(VI) concentration to 0.1 M, which is a usual phenomenon for heterogeneous catalytic processes of the adsorption nature. All further kinetic experiments were performed at the initial U(VI) concentration of 0.05 M, i.e., under the conditions when the slow reaction follows a first-order law with respect to [U(VI)]. The first-order rate constants were calculated by the rate equation

$$-dC/d\tau = k_1 C. \tag{6}$$

The constants k' and k_1 were calculated from the results of three independent kinetic experiments. The results for various catalysts and experimental conditions are listed in Table 3. It should be noted that the accuracy in determination of the constant k' of the fast

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Fig. 2. Kinetic curves of reduction of various amounts of $[U(VI)]_0$ in 0.5 M H₂SO₄ in the presence of 0.2 M N₂H₄ and 0.05 g ml⁻¹ of 1% Pd/SiO₂ (A) at 70°C. $[U(VI)]_0$, M: (1) 0.2, (2) 0.1, (3) 0.05, (4) 0.02, and (5) 0.01.

stoichiometric reaction is relatively low. This is associated with rather arbitrary determination of the boundary of the fast reaction section in the semilog kinetic curve. The error in the determination of the constant k_1 of the slow catalytic reaction does not exceed $\sim 10\%$, which is typical for kinetic measurements. The data of Table 3 allow us to analyze the main kinetic relationships of the catalytic reduction of U(VI)with hydrazine in the presence of the palladium catalyst. In spite of substantial scattering in k' values, their analysis allows certain conclusions about the character of the process. The temperature dependences of k'measured for the catalysts 1% Pd/SiO2 (A) and 1% Pd/SiO₂ (B) correspond to apparent activation energies of ~ 17 and ~ 20 kJ mol⁻¹, respectively, which is typical of diffusion-controlled processes (activation energy $\sim 19 \text{ kJ mol}^{-1}$ [10]). As expected, the rate of such a reaction is practically independent of the reductant (hydrazine) concentration, since the concentration of the active radicals formed during conditioning the catalyst surface is determined only by the volumetric concentration of the active centers of the catalysis. Certain decrease in k' with increasing [H₂SO₄] is probably caused by a decrease in the UO_2^{2+} mobility in the solution with an increase in the ionic strength, which is typical of processes controlled by the mass transfer.

The main kinetic relationships of the U(VI) catalytic reduction with hydrazine in sulfuric acid solutions were determined in the presence of the 1% Pd/SiO₂ (A) catalyst. An increase in the catalyst content of the reaction mixture is accompanied by a proportional increase in the rate of the slow catalytic reaction (Table 1), which is characteristic for heterogeneouscatalytic processes. An increase in [N₂H₄] within the 0.05-0.3 M range causes a monotonic increase in k_1 .

$S:L,\ g\ ml^{-1}$	[N ₂ H ₄], M	[H ₂ SO ₄], M	<i>T</i> , °C	$k', 1 \text{ mol}^{-1} \text{ min}^{-1}$	$k_1, \text{ min}^{-1}$
1% Pd/SiO ₂ (A)					
0.01	0.2	0.5	60	_	$7.1 imes 10^{-4}$
0.02	0.2	0.5	60	_	1.66×10^{-3}
0.05	0.2	0.5	60	_	5.61×10^{-3}
0.1	0.2	0.5	60	_	2.97×10^{-2}
0.2	0.2	0.5	60	_	6.18×10^{-2}
0.05	0.05	0.3	70	4.0	2.50×10^{-2}
0.05	0.1	0.3	70	3.9	3.67×10^{-2}
0.05	0.2	0.3	70	4.3	4.97×10^{-2}
0.05	0.3	0.3	70	4.2	5.90×10^{-2}
0.05	0.4	0.3	70	4.3	6.92×10^{-2}
0.05	0.1	0.1	70	4.0	5.82×10^{-2}
0.05	0.1	0.5	70	3.7	2.92×10^{-2}
0.05	0.1	0.7	70	3.2	2.57×10^{-2}
0.05	0.2	0.3	40	2.5	4.39×10^{-3}
0.05	0.2	0.3	50	3.2	1.08×10^{-2}
0.05	0.2	0.3	60	4.0	2.54×10^{-2}
			1% Pd/SiO ₂	(B)	
0.05	0.2	0.3	40	2.5	2.69×10^{-3}
0.05	0.2	0.3	50	3.5	5.84×10^{-3}
0.05	0.2	0.3	60	4.3	1.77×10^{-2}
0.05	0.2	0.3	70	5.2	4.40×10^{-2}
4% Pd/SiO ₂ (A)					
0.05	0.2	0.3	32	_	3.73×10^{-2}
0.05	0.2	0.3	40	_	5.73×10^{-2}
0.05	0.2	0.3	50	_	9.12×10^{-2}
0.05	0.2	0.3	60	_	1.25×10^{-1}
0.05	0.2	0.3	70	_	$1.70 imes 10^{-1}$
$4\% \text{ Pd/SiO}_2(B)$					
0.05	0.2	03	325	_	3.87×10^{-2}
0.05	0.2	0.3	50	_	7.97×10^{-2}
0.05	0.2	0.3	60	_	1.29×10^{-1}
0.05	0.2	0.3	70	_	1.22×10^{-1} 1.73×10^{-1}
0.05	0.2	0.5	/0	L	1.73 ~ 10

Table 3. Catalytic reduction of U(VI) with hydrazine in sulfuric acid solutions in the presence of palladium catalysts

With a further increase in $[N_2H_4]$ to 0.4 M, the rate of U(VI) reduction does not increase. In the log-log coordinates, within the $[N_2H_4]$ 0.05–0.3 M range, this dependence is a straight line with a slope close to



Fig. 3. Rate of catalytic reduction of 0.05 M U(VI) in the presence of 0.3 M H_2SO_4 and 0.05 g ml⁻¹ of 1% Pd/SiO₂ (A) at 70°C as a function of hydrazine concentration.

0.5 (Fig. 3), which can be interpreted as the reaction order with respect to N_2H_4 [11, 12]. The order of 0.5 reflects the adsorption type of the process and follows from the equation of the Langmuir isotherm for the reactant chemisorption on two neighboring catalysis centers [13]. A decrease in the reaction order with respect to hydrazine from 1/2 to 0 at $[N_2H_4] > 0.3$ M is caused by saturation of the catalysis centers with the adsorbed N_2H_4 molecules, which is typical for heterogeneous catalytic reactions in solutions [1].

With an increase in the H₂SO₄ concentration from 0.1 to 0.7 M at $[U(VI)]_0 = 0.05$, $[N_2H_4 \cdot H_2SO_4] = 0.1$ M, and 70°C in the presence of 0.1 g ml⁻¹ of 1% Pd/SiO₂ (A), k_1 substantially decreases, which can be

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attributed to an increase in the yield of U(VI) sulfate complexes which are less reactive with respect to the reductant as compared to hydrated uranyl ion. The apparent reaction order with respect to the H₂SO₄ concentration, calculated from the slope of the straight line in the ln [H₂SO₄]–ln k_1 coordinates, is -0.42. It should be noted that the intervals of H₂SO₄ and N₂H₄ concentrations examined in this study are relatively narrow, since at [H₂SO₄] < 0.1 M U(IV) undergoes hydrolysis, and the upper limit of the H₂SO₄ and N₂H₄ concentrations is determined by the solubility of hydrazine sulfate, decreasing with an increase in [H₂SO₄].

The experimental data on the kinetics and stoichiometry of the catalytic reduction of U(VI) with hydrazine in sulfuric acid in the presence of palladium catalyst allow certain assumptions concerning the reaction mechanism. Uranyl ions are reduced in reactions with two kinds of reducing species. These are radicals $N_2H_3^*$ and hydrogen atoms H chemisorbed by Pd atoms. The formation of these species can be schematically presented by Eq. (2) or, more accurately, by the following scheme taking into account the reaction order of 1/2 with respect to hydrazine concentration:

$$2Pd + N_2H_4 \rightleftharpoons Pd \cdots H - NH - NH - H \cdots Pd$$
$$\rightleftharpoons Pd(H) + Pd(N_2H_3^{\bullet}). \tag{7}$$

In view of the above-noted tendency of Pd atoms to form with hydrogen fairly strong hydride-type compounds [9], we can suggest that H atoms are less reactive than the adsorbed radicals $N_2H_3^{\bullet}$ with respect to uranyl ions. The latter radicals rapidly react with U(VI) following Eq. (3), with the subsequent recombination of H_2N-N^{\bullet} radicals in the reaction chain:

$$2H_2N-N \rightarrow H_2N-N=N-NH_2 \rightarrow N_2 + N_2H_4.$$
 (8)

Less reactive reducing Pd(H) species slowly react with U(VI):

$$Pd(H) + UO_2^{2+} \rightarrow UO_2^{+} + H^{+} + Pd.$$
 (9)

Uranium(V) rapidly disproportionates into U(VI) and U(IV):

$$2UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O, \qquad (10)$$

and the released surface Pd atoms restore their ability to chemisorb new hydrazine molecules and continue the catalytic reaction. In other words, in the system considered, the heterogeneous-catalytic redox cycle

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Fig. 4. Mechanism of U(VI) catalytic reduction with hydrazine on the palladium catalyst.

involving the surface Pd atoms is realized (Fig. 4). In this cycle, the reaction of chemisorbed hydrogen atoms with uranyl ions is the slow, rate-determining stage.

Summation of the equations of intermediate reactions (7), (3), and (8)–(10) with regard to stoichiometric coefficients gives the total stoichiometric equation of the process:

$$2UO_2^{2+} + N_2H_4 + 4H^+ = 2U^{4+} + N_2 + 4H_2O$$
, (11)

which is identical to experimental Eq. (1), confirming the adequacy of the suggested mechanism.

The comparison of the catalytic activity of various palladium catalysts (Table 1) shows that the catalyst 1% Pd/SiO₂ (A) prepared by calcination of the silica support with the precursor applied, followed by reduction with hydrogen, exhibits substantially higher activity in the reduction of U(VI) than the catalyst 1% Pd/SiO₂ (B) prepared without calcination. At the same time, the catalysts 4% Pd/SiO₂ (A) and 4% Pd/SiO₂ (B) exhibit virtually the same activity. It is of interest that the catalyst 1% Pd/SiO₂ (B), in spite of higher degree of dispersion of the active metal, is substantially less active at the same S:L ratio than the 1% Pd/SiO₂ (A) catalyst. To quantitatively estimate the specific activity of catalysts, we used the number of turnovers r, min⁻¹, i.e., 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 mol l⁻¹ min⁻¹ units; V, volume of the reaction mixture in liters; and N, number of moles of the surface Pd atoms. The number of moles of the surface Pd atoms involved in the heterogeneous-catalytic process was calculated from the catalyst weight, Pd percent content on the support, and metal dispersity found by electron microscopy. The U(VI) reduction follows the first-order law with respect to $[UO_2^{2+}]$. The reaction rate decreases with the progress of the reaction. Therefore, as parameter ω we took the change in hydrazine concentration in 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., $\omega = C_0 \tau_{1/2}$ [C_0 is the U(VI) initial concentration]. The turnover numbers calculated for

Table 4. Influence of the size of Pd nanoaggregates on the specific activity of Pd/SiO₂ catalysts in the reduction of U(VI) with hydrazine in sulfuric acid solutions at $[U(VI)]_0 = 0.05$, $[N_2H_4] = 0.2$, $[H_2SO_4] = 0.3$ M, and $T = 60^{\circ}C$

Catalyst	$d_{\rm vs}$, nm	D	r, \min^{-1}
1% Pd/SiO ₂ (A)	12.9	0.086	2.24
1% Pd/SiO ₂ (B)	8.8	0.130	1.06
4% Pd/SiO ₂ (A)	12.7	0.088	2.18
4% Pd/SiO ₂ (B)	12.3	0.091	2.17

Table 5. Apparent activation energies E^* of U(VI) reduction with hydrazine in sulfuric acid solutions in the presence of various palladium catalysts at $[U(VI)]_0 = 0.05$, $[N_2H_4] = 0.2$, $[H_2SO_4] = 0.3$ M, and S : L = 0.05 g ml⁻¹

Catalyst	d _{vs} , nm	E^* , kJ mol ⁻¹
1% Pd/SiO ₂ (A)	12.9	77.5 ± 0.8
1% Pd/SiO ₂ (B)	8.8	85.2 ± 5.3
4% Pd/SiO ₂ (A)	12.7	34.5 ± 1.5
4% Pd/SiO ₂ (B)	12.3	35.4 ± 1.6

various catalysts at $[U(VI)]_0 = 0.05$, $[N_2H_4] =$ 0.2, $[H_2SO_4] = 0.3$ M, and $T = 60^{\circ}C$ are listed in Table 4. The data obtained show that the specific (per surface atom) activity of the palladium catalysts is determined only by the size of nanoaggregates of the active metal and is independent of the metal content on the support, i.e., the surface Pd atoms located on large crystallites exhibit higher catalytic activity. Thus, the catalytic reduction of U(VI) with hydrazine in sulfuric acid solutions belongs to structure-sensitive catalytic processes. The negative size effect is observed. These results can be interpreted on the bases of the above-described mechanism of the catalytic process. Indeed, a decrease in the nanoaggregate size should increase the fraction of the apical and edge low-coordinate atoms [14]. It is reasonable to expect that the energy of the chemical bond between Pd and chemisorbed H atom on such coordination-unsaturated centers of the catalysis is higher than on Pd atoms located on the crystallite faces. The chemisorbed H atom is probably the active intermediate that reduces uranyl. Its activity is determined by the energy of the Pd–H bond: the higher this energy, the more difficult is the oxidation and hence the lower is the catalyst activity.

The temperature dependences of rates of catalytic reduction of U(VI) with hydrazine in sulfuric acid

solutions were measured in the presence of various palladium catalysts. In Arrhenius coordinates, these dependences are straight lines within the 30-70°C range. The corresponding values of the apparent activation energy are listed in Table 5. As can be seen, under equal other conditions, the activation energies depend on the size of Pd particles and on the metal content on the support. The observed decrease in the apparent activation energy of U(VI) reduction on 1% Pd/SiO₂ catalysts with increasing size of Pd nanoaggregates reflects the negative size effect and is determined by a decrease in the Pd-H bond energy in the intermediates on the catalyst surface. Since the experimental apparent activation energy of heterogeneous-catalytic process is related to the true activation energy by the formula $E^* = E_{tr} - \lambda$ (λ is the integral heat of adsorption) [15], it is clear that an increase in the metal content on the support at a constant composition of the reaction mixture should lead to a decrease in E^* because of an increase in the integral heat of reactant adsorption with a decrease in the coverage of the catalyst surface.

Unfortunately, we cannot unambiguously answer why palladium catalysts effectively initiating U(VI)reduction with hydrazine in sulfuric acid solutions are inactive in nitric acid media, in contrast to platinum catalysts [1]. The possible reason of this phenomenon is different reactivity of reducing intermediates formed by sorption of hydrazine molecules on the active centers of the catalyst with respect to the competing oxidizing species, UO_2^{2+} and HNO_3 . Presumably, N₂H₃ radicals and H atoms chemisorbed on the surface Pd atoms react mainly with HNO₃ molecules and nitronium ions NO_2^+ . This leads to progressive oxidative decomposition of hydrazine in the presence of palladium catalyst. In the process, U(VI) is not reduced. A different pattern is observed with platinum catalysts, when the reducing species are N₂H₄ molecules adsorbed on the surface Pt atoms. In this case, the U(VI) reduction probably proceeds via electron transition through a Pt-Pt metal bridge between hydrazine molecule and hydrated uranyl ion adsorbed on the neighboring catalytic centers [16]. The $N_2H_3^{\bullet}$ radical formed by one-electron transfer probably does not interact with the catalyst surface, and its reactivity in the solution can differ from that of N₂H₃ radical chemisorbed on surface Pd atoms. The free radicals can react in the solution with both HNO_3 and U(VI), which results in complex stoichiomerty of the reduction of U(VI) with hydrazine in HNO3 solution in the presence of platinized catalysts [16, 17]. The nature of this phenomenon is not fully understood and may

be determined by both thermodynamic and kinetic factors.

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