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MECHANISMS
OF CATALYTIC REACTIONS

Characterization of New Catalysts Based on Uranium Oxides

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Abstract—Catalysts based on uranium oxides were systematically studied for the first time. Catalysts containing various amounts of uranium oxides (5 and 15%) supported on alumina and mixed Ni–U/Al_2O_3 catalysts were synthesized. The uranium oxide catalysts were characterized using the thermal desorption of argon, the low-temperature adsorption of nitrogen, X-ray diffraction analysis, and temperature-programmed reduction with hydrogen and CO. The effects of composition, preparation conditions, and thermal treatment on physicochemical properties and catalytic activity in the reactions of methane and butane oxidation, the steam and carbon dioxide reforming of methane, and the partial oxidation of methane were studied. It was found that a catalyst containing 5% U on alumina calcined at 1000°C was most active in the reaction of high-temperature methane oxidation. For the Ni–U/Al_2O_3 catalysts containing various uranium amounts (from 0 to 30%), the introduction of uranium as a catalyst constituent considerably increased the catalytic activity in methane steam reforming and partial oxidation.

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INTRODUCTION

Uranium oxides form the basis of fuel elements; they are also successfully used in other areas of science and technology [1]. The unique properties of the U–O system are also highly attractive to catalysis. Uranium is characterized by a number of oxidation states. Many polymorphic modifications and solid solutions occur in the U–O system; there are a variety of compounds with variable composition and metastable phases. The occurrence of at least 10 uranium oxides and 14 of their modifications was reported [2, 3].

Hutchings et al. [4–16] studied the catalytic properties of uranium oxides in the low-temperature catalytic oxidation of volatile organic compounds (VOCs), including organochlorine compounds. Thus, Hutchings et al. [6] demonstrated the possibility of almost complete (99.9%) VOC conversion on uranium oxide catalysts at 100% selectivity for CO_2 over the temperature range 300–400°C depending on VOC composition. For comparison, analogous results were obtained on Co_3O_4, which is the most active catalyst of well-known catalysts for VOC oxidation [17], at 600°C. Moreover, unlike all of the well-known catalysts, including Co_3O_4 and catalysts based on noble metals [18], uranium oxide catalysts were found to exhibit uniquely high resistance to the poisonous effect of halogens. According to the preliminary data of Hutchings and coworkers, uranium oxide catalysts retained high activity in the presence of sulfur-containing impurity compounds and water vapor. Their enhanced thermal stability was also noted.

The 10 mol % U_3O_8/SiO_2 supported catalyst was studied in the publications cited above. Hutchings et al. demonstrated that the supporting of U_3O_8 on SiO_2 increased the temperature of complete VOC conversion by approximately 50 K, as compared with that on pure U_3O_8. Nevertheless, in this case, the activity of the catalyst remained higher than that of Co_3O_4. The introduction of transition metal (Co, Cu, Cr, etc.) oxides as modifying additives increased the activity of supported uranium catalysts to the level of bulk U_3O_8. In this case, selectivity for CO_2 increased to almost 100%. This effect was most pronounced in the case of the addition of Cu [6, 9].

An analysis of the patent literature over the past 40 years allowed us to conclude that a great number of chemical processes effectively occur with the participation of catalysts based on uranium oxides.

Uranium-containing catalysts are active in the following processes: the hydrotreatment of hydrocarbon raw materials [19, 20]; the Fischer–Tropsch synthesis of hydrocarbons [21–24]; the steam reforming of hydrocarbons [25, 26]; the synthesis of liquid hydrocarbons from methanol [27]; and the manufacture of CO, CH_4, and H_2 from higher hydrocarbons [28–30]. Because mixed multicomponent uranium oxide catalysts with the specified strengths of oxygen bonds can be synthesized, they are successfully used in the industrial processes of ammoxidation and partial oxidation [31–36].

The development of new catalysts based on uranium oxides is of considerable current interest in the processes of hydrogen energetics, petroleum refining, petroleum chemistry, fine organic synthesis, and gas purification for the removal of harmful impurities including halogen- and sulfur-containing VOCs.

This work is the first publication of a series of systematic studies initiated in the past few years. It is devoted to the synthesis and characterization of catalysts containing individual uranium oxides and mixed compositions with transition metal oxides supported onto alumina. Catalytic activity was measured for comparatively simple reactions: deep hydrocarbon oxidation, steam and carbon dioxide reforming of methane, and the partial oxidation of methane to synthesis gas.

EXPERIMENTAL

Synthesis of Catalysts

The uranium oxide catalysts supported on alumina were prepared by the incipient wetness impregnation of a spherical γ-Al_2O_3 support (particle size of 1.0–1.6 mm), which was prepared by hydrocarbon–ammonia molding [37], with aqueous solutions of uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$). The catalyst after impregnation was dried at 100°C and calcined at 600, 800, and 900°C for 4 h or at 1000°C for 3 h. The uranium content of the UO_x/Al_2O_3 oxide catalysts was calculated as the amount of uranium element in wt %. For convenience, the samples containing 5 and 15 wt % U are referred to as $5U/Al_2O_3$ and $15U/Al_2O_3$, respectively.

The nickel–uranium catalysts were prepared by the impregnation of U/Al_2O_3 catalysts calcined at 500 and 1000°C with a solution of nickel nitrate, which was taken in an amount required for 10 wt % Ni in the mixed catalyst. For comparison, a 10% Ni/Al_2O_3 catalyst was prepared by the impregnation of the support with a solution of nickel nitrate. The catalysts were calcined at 850°C in air. The uranium contents of the prepared catalysts were 0, 4.3, 13, and 26 wt %. Henceforth, the concentration of uranium (in wt %) before the stage of supporting nickel and the temperature of calcination after impregnation are specified in catalyst designations, for example, Ni–5U(500)/Al_2O_3; that is, Ni was supported on a uranium–alumina catalyst containing 5% U and calcined at 500°C.

Catalyst Characterization

The synthesized catalysts were characterized by the thermal desorption of argon, the low-temperature adsorption of nitrogen, X-ray diffraction (XRD) analysis, and temperature-programmed reduction (TPR) with hydrogen and CO.

The specific surface areas (S_{sp}, m^2/g) of samples were measured using the thermal desorption of argon.

The pore structure of catalysts was studied on an ASAP-2400 instrument using nitrogen adsorption at −196°C.

The XRD analysis was performed on an HZG-4 instrument with CuK_α radiation over the 2θ angle range 20°–80° at a scanning rate of 1 deg/min. Phases were identified using the JCPDS XRD database.

The TPR experiments with catalyst samples were performed in a flow reactor. The catalyst samples were trained in a flow of oxygen at 500°C immediately before experiments. In the TPR measurements, the samples were heated from 40 to 900°C at a rate of 10 K/min. The flow rate of a working mixture was 40 ml/min. The composition of the mixture was 10% hydrogen in argon or 10% CO in helium. The reduction products (water or CO_2) were frozen in a low-temperature trap. A thermal-conductivity detector (TCD) was used for the detection of hydrogen or CO consumption.

Catalytic Activity

The catalytic activity in the deep oxidation reactions of methane and butane was studied in a quartz tube flow reactor. The reactor temperature was varied from 200 to 700°C in the case of CH_4 or from 100 to 700°C in the case of C_4H_{10}. The catalyst loading was 1 cm^3. The initial reaction mixture containing 1 vol % CH_4 in air was supplied to the reactor at a rate of 16.7 cm^3/min, which corresponded to a space velocity of 1000 h^{-1}. The reaction mixtures before and after the reactor were analyzed on an LKhM-8MD chromatograph with a TCD. The gas mixtures were separated on a NaX column at room temperature.

The reactions of methane steam and carbon dioxide reforming were performed in a flow reactor in a laboratory setup over the temperature range 700–850°C. The synthesized Ni–U/Al_2O_3 catalysts were tested in the reactions of methane steam (C_{CH_4} = 20 vol %, C_{H_2O} = 60 vol %, C_{Ar} = 20 vol %, and space velocity of 50000 h^{-1}) and carbon dioxide reforming (C_{CH_4} = 20 vol %, C_{CO_2} = 20 vol %, C_{Ar} = 60 vol %, and space velocity of 50000 h^{-1}).

The catalytic activity in the reaction of partial methane oxidation to synthesis gas was studied in a flow setup (C_{CH_4} = 20 vol %, C_{O_2} = 10 vol %, C_{Ar} = 70 vol %, space velocity of 50000 h^{-1}, and reactor temperature of 550–800°C). The reaction mixtures were analyzed on a Kristall 2000M gas chromatograph equipped with a thermal-conductivity and a flame-ionization detector.

RESULTS AND DISCUSSION

Individual Uranium Oxides Supported on Alumina (U/Al_2O_3)

Physicochemical properties of U/Al_2O_3 catalysts. Tables 1 and 2 summarize the main physicochemical properties (S_{sp}; phase composition) of catalyst samples

Table 1. Dependence of the properties of the $5U/Al_2O_3$ catalyst on the conditions of thermal treatment

Conditions of thermal treatment	S_{sp}, m^2/g	XRD data	Catalyst color
Support			
550°C in air	170	γ-Al_2O_3 ($a = 7.920$ Å)	White
Catalysts			
500°C in air	160	γ-Al_2O_3 ($a = 7.920$ Å)	Yellowish orange
600°C in air	167	″	Yellowish orange
600°C in H_2 + Ar	154	″	Gray
800°C in air	110	γ-Al_2O_3	Yellowish brown
900°C in air	78	δ-Al_2O_3 γ-Al_2O_3	Yellowish brown
1000°C in air	40	θ-Al_2O_3, α-U_3O_8 (31-1424)*; α-$UO_{3.01}$ (46-947)* or α-$UO_{2.92}$ (46-948)* can occur	Gray with beige spots
1100°C in air	33	θ-Al_2O_3, α-Al_2O_3 (traces), α-U_3O_8 (31-1424)*; α-$UO_{3.01}$ (46-947)* or α-$UO_{2.92}$ (46-948)* can occur	Greenish gray

* Compound number in the JCPDS database.

Table 2. Dependence of the properties of the $15U/Al_2O_3$ catalyst on the conditions of thermal treatment

Conditions of thermal treatment	S_{sp}, m^2/g	XRD data	Catalyst color
Drying in air	–	γ-Al_2O_3	Yellowish orange
600°C in air	122	″	Yellowish orange
800°C in air	60	γ-Al_2O_3, α-U_3O_8 (31-1424)*; α-$UO_{3.01}$ (46-947)* or α-$UO_{2.92}$ (46-948)* can occur	Yellowish green
900°C in air	43	δ-Al_2O_3, α-U_3O_8 (31-1424)*; α-$UO_{3.01}$ (46-947)* or α-$UO_{2.92}$ (46-948)* can occur	Dark green
1000°C in air	32	θ-Al_2O_3, α-U_3O_8 (31-1424)*; α-$UO_{3.01}$ (46-947)* or α-$UO_{2.92}$ (46-948)* can occur	Dark green

* Compound number in the JCPDS database.

containing 5 and 15% U supported on alumina and calcined at various temperatures.

Tables 1 and 2 show changes in the specific surface areas of catalyst samples depending on thermal treatment conditions. The results suggest that the specific surface area of catalysts decreased with calcination temperature in the samples of both $5U/Al_2O_3$ and $15U/Al_2O_3$. It is most likely that, as the calcination temperature was increased to 800°C, the specific surface area of catalysts decreased because of changes in the pore structure of the support due to the observed phase transformations of alumina. After thermal treatment at 1000°C, the decrease in the specific surface area was also due to the agglomeration of the uranium oxide phase.

Table 3 summarizes the effect of calcination temperature on the pore volume and specific surface area of the $5U/Al_2O_3$ catalyst (600, 1000, and 1100°C) as studied using the low-temperature adsorption of nitrogen

Table 3. Dependence of the texture properties of $5U/Al_2O_3$ catalyst samples on the temperature of calcination (T_{calcin})

T_{calcin}, °C	S_{sp} (Ar), m^2/g	S_{sp} (N_2), m^2/g	V_{pore} (N_2), cm^3/g
600	167	165	0.42
800	110	116	0.41
1000	40	48	0.35
1100	33	30	0.13

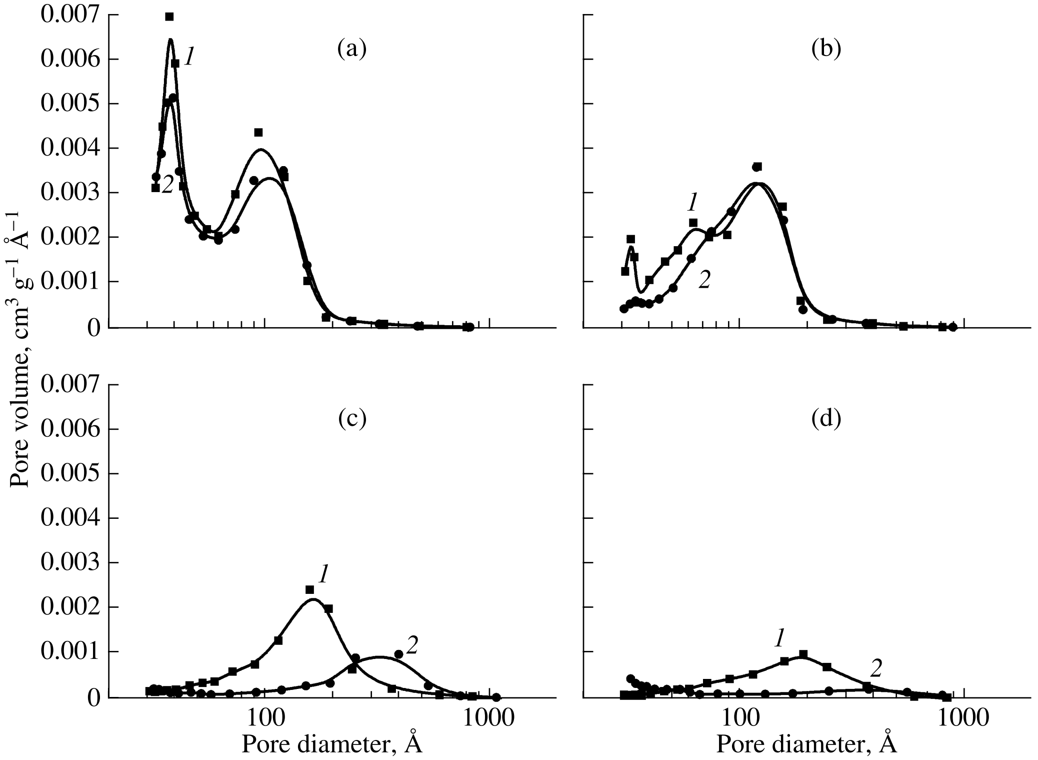

Fig. 1. Pore-size distribution in the samples of (*1*) the support and (*2*) the 5U/Al_2O_3 catalyst calcined at (a) 600, (b) 800, (c) 1000, and (d) 1100°C.

and argon. Figure 1 shows pore-size distributions (as differential functions) at various temperatures of calcination of the catalyst and the parent support. The specific surface area characteristics are consistent with data obtained by the thermal desorption of argon (Table 3). The pore structure of catalysts changed as the calcination temperature was increased. The dynamics of changes in the specific surface area and pore volume was different. In the catalyst sample calcined at 600°C, pores of size from 30 to 100 Å mainly occurred. As the calcination temperature was increased to 1000°C, fine pores disappeared, particles that formed the catalyst framework became coarser, and pores of size from 200 to 1000 Å appeared. The total pore volume decreased only slightly, whereas the specific surface area, which depends on the amount of fine pores, dramatically decreased (Table 3). Thermal treatment at 1100°C resulted in the agglomeration of coarse pores; the specific surface area decreased to a lesser extent, whereas the pore volume decreased considerably, as compared with corresponding changes over the calcination temperature range 600–1000°C.

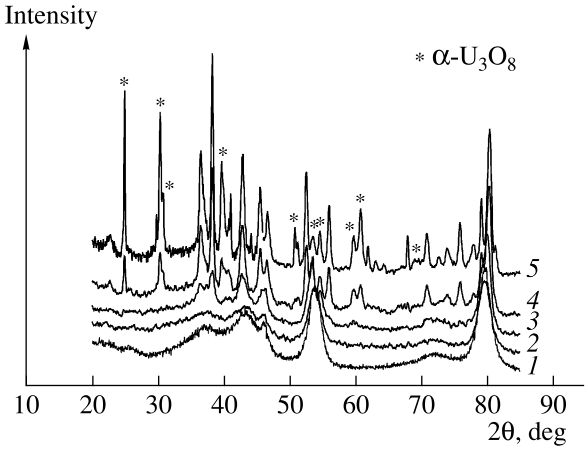

Fig. 2. Diffraction patterns of (*1*) the support and 5U/Al_2O_3 catalyst samples calcined at (*2*) 600, (*3*) 900, (*4*) 1000, and (*5*) 1100°C.

Figures 2 and 3 show the diffraction patterns of catalysts from the 5U/Al_2O_3 and 15U/Al_2O_3 series. The samples of 5U/Al_2O_3 calcined at 600°C (Fig. 2) exhibited only lines due to the γ-Al_2O_3 support. This can be related to the fact that, at a ≤5% uranium content of the catalyst, uranium oxide occurred as a highly dispersed phase with a particle size smaller than 5.0 nm, and it was not detected by XRD analysis, which was used in this study.

As the calcination temperature was increased to 900°C, polymorphic transformations occurred in the support. Because of this, the diffraction pattern exhibited lines due to δ-Al_2O_3 (the most characteristic region 35°–37°) in addition to the lines of γ-Al_2O_3. At 1000–1100°C, the lines of a practically pure θ-Al_2O_3 phase

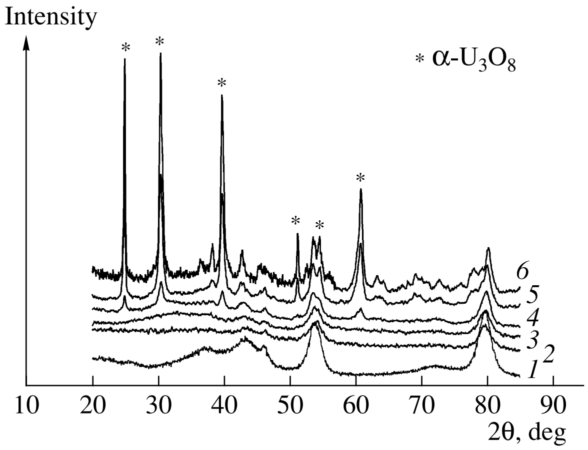

Fig. 3. Diffraction patterns of (*1*) the support and $15U/Al_2O_3$ catalyst samples (*2*) dried and calcined at (*3*) 600, (*4*) 800, (*5*) 900, and (*6*) 1000°C.

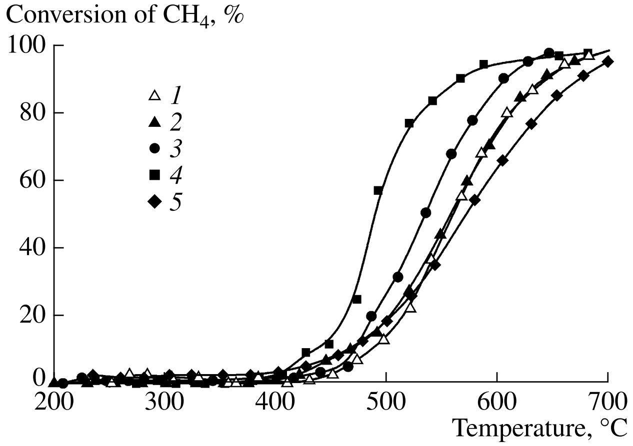

Fig. 4. The temperature dependence of methane conversion in the deep oxidation reaction on the $5U/Al_2O_3$ catalyst calcined (*1*) in a flow of 30 vol % H_2 + Ar at 600°C or in air at (*2*) 600, (*3*) 900, (*4*) 1000, and (*5*) 1100°C.

and uranium oxide appeared. It is most likely that the latter is U_3O_8 (31-1424), whose characteristic lines appear at the angles 25° and 30°. The other lines of the U_3O_8 phase appear at the angles 30.92°, 39.61°, 40.11°, 51.16°, 53.37°, 54.59°, 59.77°, 60.60°, 60.91°, and 68.81°. Table 1 shows other conceivable uranium oxide compounds; however, the final identification of these compounds is difficult to perform because of the overlapping of support and uranium oxide lines.

The diffraction patterns of $15U/Al_2O_3$ samples (Fig. 3) are analogous to those of $5U/Al_2O_3$ samples and consistent with the polymorphic transformations of alumina, which occur in the course of the thermal treatment of catalysts at 900°C or higher. In the $15U/Al_2O_3$ samples, lines corresponding to uranium compounds appeared after calcination at 800°C.

An increase in the calcination temperature above 1000°C for $5U/Al_2O_3$ samples or 800°C for $15U/Al_2O_3$ samples resulted in a dramatic increase in the intensities of uranium oxide lines. The effect observed can be due to the agglomeration of the highly dispersed active component of a catalyst at high temperatures with the formation of a coarsely dispersed phase of uranium oxides with a particle size greater than 50 nm.

Catalytic activity of U/Al_2O_3 in the deep oxidation of methane. Figures 4 and 5 show the temperature dependence of the degree of methane conversion. The effect of thermal activation was observed in catalysts with a low uranium content (5 wt %) (Fig. 4). The activity of a catalyst increased as the calcination temperature was increased from 600 to 1000°C. The catalyst calcined at 1000°C exhibited the highest activity. A further increase in the calcination temperature to 1100°C resulted in a considerable decrease in catalytic activity. This change in catalytic activity can be explained by the occurrence of the optimum particle size of the active component formed upon a moderate agglomeration of highly dispersed particles. As the calcination temperature was increased to 1100°C, the subsequent agglomeration with the formation of coarse particles of uranium oxides resulted in deactivation.

In catalysts with a high uranium content (15 wt %) (Fig. 5), the catalysts calcined at 600 and 800°C were most active. That is, particles with an optimum size were formed at lower temperatures, whereas an increase in the calcination temperature to 900 or 1000°C resulted in a decrease in catalytic activity.

Catalytic activity of U/Al_2O_3 in the deep oxidation of butane. The samples of U/Al_2O_3 catalysts containing 5 and 15% U calcined at 600 and 800°C were studied in the reaction of deep oxidation of butane. For comparison, the samples of bulk U_3O_8, which were prepared by precipitation from aqueous solutions of uranyl nitrate [38] and calcined at 600 and 800°C, were also studied (Fig. 6). A comparison between data obtained

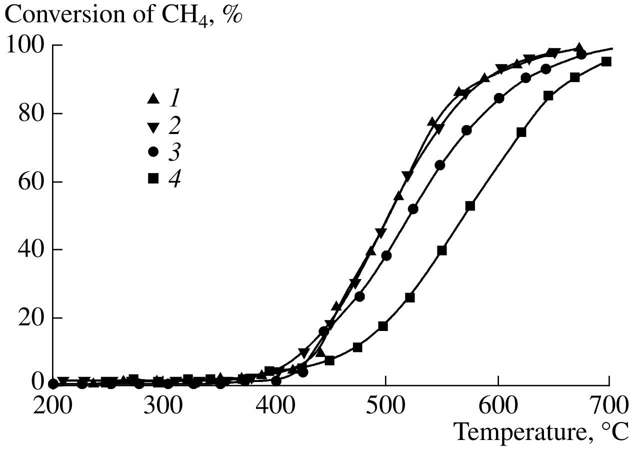

Fig. 5. The temperature dependence of methane conversion in the deep oxidation reaction on the $15U/Al_2O_3$ catalyst calcined in air at (*1*) 600, (*2*) 800, (*3*) 900, and (*4*) 1000°C.

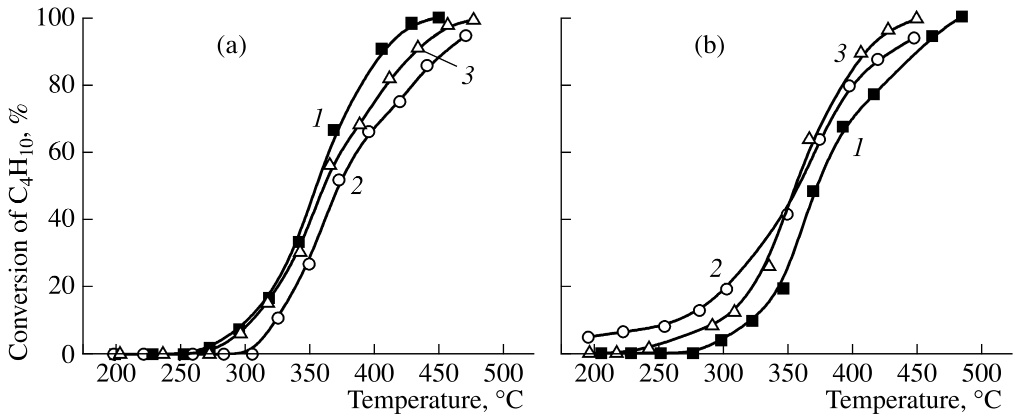

Fig. 6. The temperature dependence of butane conversion in the deep oxidation reaction on catalysts calcined at (a) 600 and (b) 800°C: (*1*) bulk U_3O_8, (*2*) $5U/Al_2O_3$, and (*3*) $15U/Al_2O_3$.

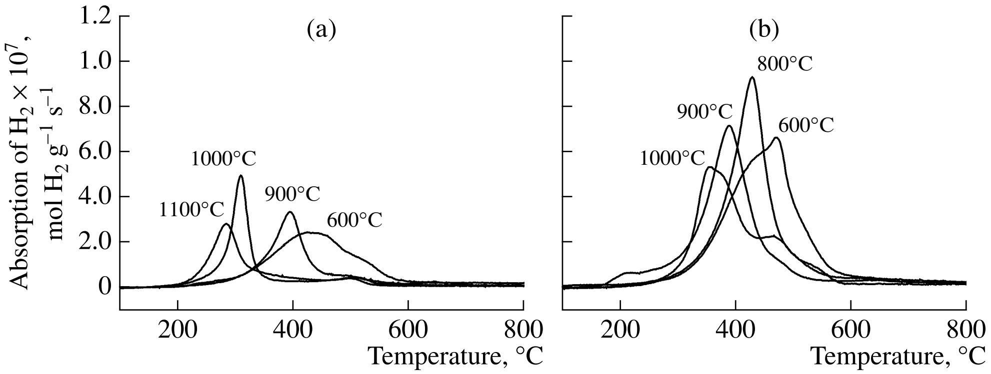

Fig. 7. TPR-H_2 curves for the samples of (a) $5U/Al_2O_3$ and (b) $15U/Al_2O_3$ catalysts calcined at various temperatures (specified in the figure).

in bulk and supported catalysts allowed us to conclude that the catalytic activity of supported samples in the reaction of butane oxidation was close to the activity of U_3O_8 or higher than the activity of the bulk sample.

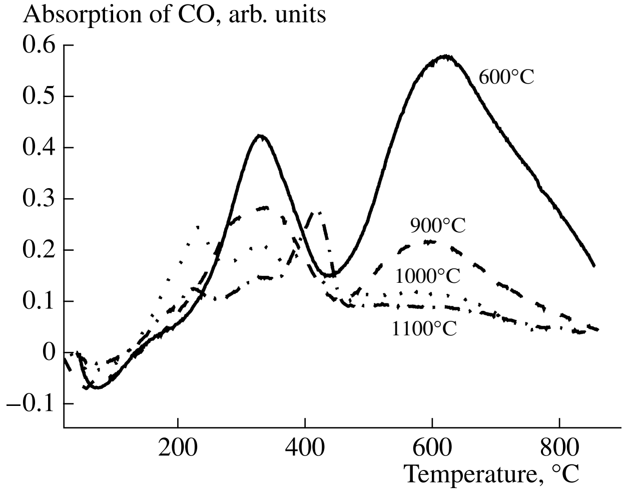

Fig. 8. TPR-CO curves for the samples of $5U/Al_2O_3$ catalysts calcined at various temperatures (specified in the figure).

TPR studies of U/Al_2O_3 catalysts. To explain the effect of the conditions of thermal treatment of supported uranium oxide catalysts on their activity in the deep oxidation of methane, we performed studies using TPR with hydrogen and CO.

Figure 7 shows the TPR curves obtained in $5U/Al_2O_3$ and $15U/Al_2O_3$ samples calcined at various temperatures. The test catalysts were characterized by hydrogen absorption peaks in the temperature range 200–600°C. The positions and intensities of these peaks depended on the amount of supported uranium and the temperature of sample calcination. An increase in the calcination temperature resulted in a decrease in the temperature of hydrogen absorption for samples containing either 5 or 15% uranium; that is, oxygen species that were more reactive appeared, and these species were removed by hydrogen at 300°C. However, the behavior can be additionally complicated because of changes in both the valence state of uranium in an oxide and the dispersion of particles, as well as due to the occurrence of phase transformations and interactions.

The samples of the $5U/Al_2O_3$ catalyst calcined at various temperatures were studied using the TPR of

Table 4. Properties of Ni–U/Al_2O_3 catalysts

Catalyst composition	S_{sp}, m^2/g	XRD data
Ni/Al_2O_3	120	Solid solution based on the γ-Al_2O_3 structure (α = 7.960 Å)
Ni-5U(500)/Al_2O_3	80	Solid solution based on the γ-Al_2O_3 structure (α = 7.956 Å)
Ni-30U(500)/Al_2O_3	25	γ-Al_2O_3 + δ-Al_2O_3 (traces); solid solution based on the γ-Al_2O_3 structure (α = 7.960 Å); α-U_3O_8 (J_{25} = 420)*
Ni-5U(1000)/Al_2O_3	33	γ-Al_2O_3 + δ-Al_2O_3 (traces); solid solution based on the γ-Al_2O_3 structure (α = 7.950 Å)
Ni-15U(1000)/Al_2O_3	19	γ-Al_2O_3 + δ-Al_2O_3 (traces); solid solution based on the γ-Al_2O_3 structure (α = 7.960 Å); α-U_3O_8 (J_{25} = 300)*
Ni-30U(1000)/Al_2O_3	12	γ-Al_2O_3 + δ-Al_2O_3 (traces); solid solution based on the γ-Al_2O_3 structure (α = 7.960 Å); α-U_3O_8 (J_{25} = 450)*

* Phase amount estimated from the integrated intensity of a line at θ = 25° in a diffraction pattern in arbitrary units.

CO. Figure 8 shows the TPR-CO curves obtained in the samples calcined at 600, 900, 1000, and 1100°C.

In a region from 110 to 450°C, all four curves exhibited a group of peaks. As the temperature of catalyst calcination was increased from 600 to 1000°C, the peak maximums of CO absorption were shifted toward low temperatures or toward increasing temperature in the sample calcined at 1100°C (Fig. 4).

A broad peak was observed in the region 450–850°C; the area of this peak decreased with increasing calcination temperature. It is most likely that the reduction of uranium oxides over a wide temperature range and the occurrence of several absorption peaks in different temperature regions suggest the occurrence of the active component of the catalysts (uranium) in various oxidation states.

Ni–U/Al_2O_3 Mixed Catalysts

Physicochemical properties. Table 4 summarizes data on the specific surface areas and phase compositions of nickel–uranium catalysts calcined at 850°C depending on the uranium content of the samples and the temperature of calcination after the stage of supporting uranium. An increase in the uranium content of the samples from 0 to 30% resulted in a considerable decrease in the specific surface areas of the catalysts: the S_{sp} of the 15% Ni/Al_2O_3 sample containing no uranium additives was 120 m^2/g, and it decreased by an order of magnitude to 12 m^2/g as the amount of uranium was increased to 30%. An increase in the temperature of calcination of a U/Al_2O_3 sample before the stage of introducing nickel from 500 to 1000°C also resulted in a decrease in the specific surface area of the final catalyst.

Changes in the phase composition of Ni–U/Al_2O_3 catalysts are analogous to those of the samples of individual uranium oxides supported on alumina. At small amounts of uranium oxides (<5%), the phase of α-U_3O_8 was not observed; it was detected only at a uranium content of the sample higher than 15%. Although the nickel content of the catalysts was high (10 wt %), the presence of NiO oxide phases and Ni metal was not detected. The high temperature of catalyst calcination (850°C) facilitated the incorporation of nickel into solid solutions based on the γ-Al_2O_3 structure; this was observed in diffraction patterns.

Table 5. Activity characteristics of catalyst samples (yields of H_2, CO, and carbon) in the carbon dioxide reforming of methane

Catalyst	Characteristic	Reaction temperature, °C	
		800	850
Ni/Al_2O_3	Yield of H_2, %	18	22
	Yield of CO, %	18	17
	Yield of carbon, %	14	14
Ni–5U(1000)/Al_2O_3	Yield of H_2, %	11	17
	Yield of CO, %	12	16
	Yield of carbon, %	5	7
Ni–15U(1000)/Al_2O_3	Yield of H_2, %	5	17
	Yield of CO, %	10	23
	Yield of carbon, %	0	1.5
Ni–30U(1000)/Al_2O_3	Yield of H_2, %	8	22
	Yield of CO, %	13	26
	Yield of carbon, %	0	0.4

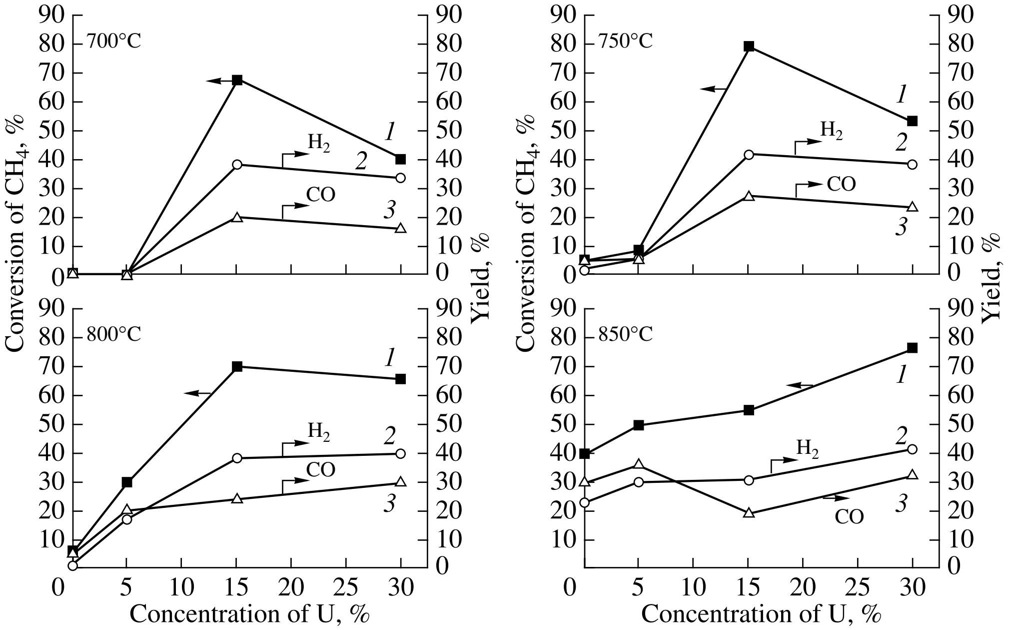

Fig. 9. Dependence of (*1*) the conversion of methane and the yields of (*2*) hydrogen and (*3*) CO in the steam reforming of CH_4 on the concentration of uranium in Ni–U/Al_2O_3 catalysts calcined at 850°C. The reaction temperatures are specified in the figure.

Catalytic activity of Ni–U/Al_2O_3 in the steam reforming of methane. The results of testing catalysts that contained 10% Ni supported on U/Al_2O_3 samples with various uranium contents (0–30%) and calcined at 1000°C in the steam reforming of methane (Fig. 9) indicate that the presence of uranium in a Ni catalyst increased the catalytic activity. In this case, the higher the uranium content of the catalyst, the higher the activity. In a sample containing 30% U, activity increased with reaction temperature to reach a maximum value at 850°C (the conversion of CH_4 was 77%). The catalysts calcined at 1000°C after supporting uranium exhibited

Table 6. Activity characteristics of catalyst samples (methane conversion and the yields of H_2 and CO) in the partial oxidation of methane

Catalyst	Characteristic	Reaction temperature, °C				
		550	600	700	750	800
Ni/Al_2O_3	X_{CH_4}, %	37	40	60	66	60
	Yield of CO, %	30	32	48	54	50
	Yield of H_2, %	20	25	40	47	40
Ni–5U(1000)/Al_2O_3	X_{CH_4}, %	54	60	72	76	80
	Yield of CO, %	46	51	65	70	73
	Yield of H_2, %	46	50	58	61	63
Ni–15U(1000)/Al_2O_3	X_{CH_4}, %	17	35	64	73	85
	Yield of CO, %	8	16	33	42	50
	Yield of H_2, %	14	27	52	60	68
Ni–30U(1000)/Al_2O_3	X_{CH_4}, %	20	40	61	71	79
	Yield of CO, %	12	23	37	44	50
	Yield of H_2, %	16	31	50	58	65

Reaction conditions: C_{CH_4} = 20 vol %; C_{O_2} = 10 vol %; C_{Ar} = 70 vol %; CH_4/O_2 = 2 : 1; space velocity, 50000 h^{-1}.

higher activities, as compared with the catalysts prepared from U/Al_2O_3 samples calcined at 500°C (the conversion of CH_4 was 47% at 850°C).

Catalytic activity of Ni–U/Al_2O_3 in the carbon dioxide reforming of methane. Table 5 summarizes the results of testing the catalyst in the carbon dioxide reforming of methane.

It is well known that the main problem in the development of catalysts for the carbon dioxide reforming of methane is catalyst deactivation as a result of coke formation. In Table 5, it can be seen that the addition of uranium as a constituent of a Ni-containing catalyst significantly decreased coke formation at a comparable value of the yield of hydrogen. The yield of carbon observed at 800°C decreased from 14% for the catalyst free of uranium additives to 0% for the catalyst containing 30% uranium.

Catalytic activity of Ni–U/Al_2O_3 in the partial oxidation of methane. Table 6 summarizes the results of testing the Ni–U/Al_2O_3 catalysts in the reaction of partial methane oxidation.

As the temperature was increased from 550 to 800°C, the activity of all of the catalyst samples (0–30 wt % U) increased. The sample with 5% uranium exhibited a higher activity at reaction temperatures of 550–750°C, as compared with samples with high uranium contents and a sample containing no uranium. As the reaction temperature was increased to 800°C, the maximum conversion of methane (85%) and the maximum yield of hydrogen (68%) were reached on a catalyst containing 15% U.

CONCLUSIONS

The systematic studies of catalysts based on uranium oxides were performed for the first time. The effects of composition, preparation conditions, and thermal treatment on the physicochemical properties and catalytic activity in the oxidation of methane, the oxidation of butane, the steam and carbon dioxide reforming of methane, and the partial oxidation of methane were studied.

It was found that the catalyst containing 5% U on alumina calcined at 1000°C exhibited the highest activity in the high-temperature oxidation of methane (T_{50} = 490°C). The effect of calcination temperature on the activity of catalysts was insignificant for the low-temperature oxidation of butane.

The introduction of uranium (from 0 to 30%) as a constituent of the Ni–U/Al_2O_3 catalyst dramatically increased catalytic activity in the reaction of methane steam reforming. Thus, on the 10% Ni/Al_2O_3 catalyst (an analogue of a commercial catalyst), the degree of methane conversion was 40% and the yield of hydrogen was 23% at 850°C and 50000 h^{-1}. At the above conditions, the degree of methane conversion and the yield of hydrogen in the reaction of methane steam reforming on the Ni–30U/Al_2O_3 catalyst were 77 and 42%, respectively.

In the reaction of the carbon dioxide reforming of methane, an increase in the uranium content of the catalyst resulted in a decrease in coke formation. The addition of 30% U as a catalyst constituent almost completely inhibited coke formation (at 850°C, the yield of carbon was ~0.4%), whereas the yield of carbon on the commercial analogue was 14% at 850°C.

The catalysts containing uranium oxides and the mixed nickel–uranium catalysts were tested in the partial oxidation of methane. The introduction of uranium as a constituent of traditional nickel-based catalysts for partial oxidation allowed us to increase the yield of hydrogen. The yield of hydrogen on uranium-containing catalysts at 800°C was as high as 65% against 40% for an analogue of a commercial Ni/Al_2O_3 catalyst under the same conditions.

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REFERENCES

1. Betti, M., *J. Environ. Radioactiv.*, 2003, vol. 64, p. 113.
2. Maiorov, A.A. and Braverman, I.B., *Tekhnologiya polucheniya poroshkov keramicheskoi dvuokisi urana* (Production of Ceramic Uranium Dioxide Powders), Moscow: Energoatomizdat, 1985.
3. *The Chemistry of the Actinide Elements*, Katz, J.J., Seaborg, G.T., and Morss, L.R., Eds., New York: Methuen, 1999.
4. Hutchings, G.J., Taylor, S.H., and Hudson, I.D., *J. Am. Chem. Soc., Dev. Pet. Chem.*, 1996, vol. 41, p. 106.
5. Hutchings, G.J., Heneghan, C.S., Hudson, I.D., et al., *ACS Symp. Ser.*, 1996, vol. 638, p. 58.
6. Hutchings, G.J., Heneghan, C.S., Hudson, I.D., et al., *Nature*, 1996, no. 384, p. 341.
7. Hutchings, G.J., Heneghan, C.S., Taylor, S.H., et al., *J. Am. Chem. Soc., Dev. Pet. Chem.*, 1997, vol. 42, p. 142.
8. Hutchings, G.J., Heneghan, C.S., O'Leary, Sh., et al., *2nd World Congr. on Environmental Catalysis*, Miami Beach, Fla., 1998.
9. Hutchings, G.J., Taylor, S.H., and Hudson, I.D., *Sci. Technol. Catal.*, 1998, p. 85.
10. Taylor, S.H., Heneghan, C.S., Hutchings, G.J., and Hudson, I.D., *Ind. Catal. News*, 1998, vol. 3, p. 4.
11. Hutchings, G.J. and Taylor, S.H., *Catal. Today*, 1999, vol. 49, p. 105.
12. Hutchings, G.J., Taylor, S.H., and Hudson, I.D., *Stud. Surf. Sci. Catal.*, 1999, vol. 121, p. 85.
13. Taylor, S.H., Heneghan, C.S., Hutchings, G.J., and Hudson, I.D., *Catal. Today*, 2000, vol. 59, p. 249.
14. Heneghan, C.S., Hutchings, G.J., O'Leary, S.R., et al., *Catal. Today*, 1999, vol. 54, p. 3.

15. Taylor, S.H. and O'Leary, S.R., *Appl. Catal.*, 2000, vol. 25, p. 137.
16. Harris, R.H., Boyd, V.J., Hutchings, G.J., and Taylor, S.H., *Catal. Lett.*, 2002, vol. 78, nos. 1-4, p. 369.
17. Golodets, G.I., *Geterogenno-kataliticheskoe okislenie organicheskikh soedinenii* (Heterogeneous Catalytic Oxidation of Organic Compounds), Kiev: Naukova Dumka, 1978.
18. Spivey, J.J. and Butt, J.B., *Catal. Today*, 1992, vol. 11, p. 465.
19. US Patent 4581344, 1986.
20. US Patent 4227993, 1980.
21. US Patent 4487851, 1984.
22. US Patent 4663305, 1987.
23. US Patent 4755536, 1988.
24. US Patent 5756419, 1998.
25. US Patent 5130114, 1992.
26. US Patent 3929624, 1975.
27. Eur. Patent 0455308, 1991.
28. US Patent 3993459, 1976.
29. US Patent 4375425, 1983.
30. US Patent 4402868, 1983.
31. US Patent 4487850, 1984.
32. US Patent 5808143, 1998.
33. Eur. Patent 0121032, 1984.
34. US Patent 4018712, 1977.
35. US Patent 3666823, 1972.
36. Patent WO 00/72962, 2000.
37. Ismagilov, Z.R., Shkrabina, R.A., and Koryabkina, N.A., *Catal. Today*, 1999, vol. 47, nos. 1–4, p. 51.
38. Zhiganov, A.N., Guzeev, V.V., and Andreev, G.G., *Tekhnologiya dioksida urana dlya keramicheskogo yadernogo topliva* (Production of Uranium Dioxide for Ceramic Nuclear Fuel), Tomsk: STT, 2002.