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Effect of the Nature of the Active Component and Support on the Activity of Catalysts for the Hydrolysis of Sodium Borohydride

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Abstract—The effect of the nature of an active component and a support on the rate of hydrolysis of aqueous sodium borohydride solutions was studied. It was found that the activity of supported catalysts, which were reduced in a reaction medium of sodium borohydride, decreased in the order Rh > Pt ≈ Ru ⩾ Pd regardless of the nature of the support (γ-Al_2O_3, a Sibunit carbon material, or TiO_2). The catalysts based on TiO_2 exhibited the highest activity. As found by UV–vis diffuse reflectance spectroscopy, the composition and structure of the supported precursor of an active component depend on the nature of the support. It is likely that rhodium clusters with different reaction properties were formed on various supports under the action of a reaction medium.

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INTRODUCTION

A solution of sodium borohydride is a safe source of pure hydrogen for portable fuel cells; it can generate to 7 wt % hydrogen. In the presence of catalysts, the liberation of hydrogen occurs even at room temperature [1]. The activity of chemically different catalysts prepared by various methods in the reaction of $NaBH_4$ hydrolysis has been studied in the last few years. In particular, the reactivity of ruthenium catalysts supported on anion-exchange resins (A-26 and IRA-400) [2, 3] and platinum group metals on various supports [4–6], as well as highly dispersed nickel and cobalt [7, 8], was studied. However, the activities of catalysts measured in the cited literature and other publications are difficult to compare with each other because the rate of hydrogen release depends on many parameters: temperature, concentration of a sodium borohydride solution, pH of the solution, design of the catalytic reactor, etc. Moreover, published data on the effect of the nature of an active component and a support on the rate of hydrolysis of sodium borohydride in the presence of supported metal catalysts formed immediately in a reaction medium of sodium borohydride are inadequate.

The aim of this work was to perform the synthesis and a comparative study of chemically different supported catalysts in the reaction of $NaBH_4$ hydrolysis: rhodium, platinum, ruthenium, and palladium supported on γ-Al_2O_3; a Sibunit carbon material; or TiO_2 (anatase). The role of the support in the formation of an active catalyst component was studied using UV–vis diffuse reflectance spectroscopy.

EXPERIMENTAL

Aqueous solutions of $RhCl_3 \cdot nH_2O$, $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, and $Ru(OH)Cl_3$ (OAO Aurat) were used for the preparation of catalysts. Water was added to a calculated weighed portion of a support, and the contents were stirred with a magnetic stirrer for 15 min. Then, a solution of a corresponding metal salt with a required concentration was added, and the mixture was additionally stirred for 15 min at room temperature. Next, the suspension was heated to 80°C, and an excess of water was evaporated with continuous stirring. After the stage of impregnation, the catalysts were dried in air at 110–130°C for 2 h. The calculated metal content was 1 wt %.

The carbon material Sibunit (KTITU, Siberian Branch, Russian Academy of Sciences) [9] with S_{BET} = 530 m^2/g and a particle size of 0.08–0.10 mm, γ-Al_2O_3 (OAO Katalizator) with S_{BET} = 170 m^2/g and the above particle size, and powdered TiO_2 samples, whose characteristics are given in Table 1, were used as supports. Rhodium catalysts on TiO_2 sample nos. 1, 2, and 3 are subsequently referred to as Rh/TiO_2-**1**, Rh/TiO_2-**2**, and Rh/TiO_2-**3**, respectively.

To study the generation of hydrogen, 98% sodium borohydride (Sigma-Aldrich) dissolved in distilled water was used. The samples of $NaBH_4$ were kept in a desiccator in order to prevent hydrate formation by the

Table 1. Physicochemical properties of TiO_2 samples

Sample	Calcination temperature, °C	S_{BET}, m^2/g	Phase composition (according to XRD data)	Dispersity, Å (according to XRD data)	Impurity concentrations, wt %
1	110	243	Anatase, 100%	110	–
2	500	79	Anatase, 96%, rutile, 4%	140	Nb, 0.04 S, 0.03 Fe, 0.22 Ca, 0.58
3	500	74	Anatase, 100%	150	Nb, 0.25 S, 3.92 Fe, 0.07 Ca, 0.01

Note: Sample 1 is a commercial product from Sigma-Aldrich (CAS 1317-70-0); sample 2 is a commercial sample from Solikamsk Magnesium Works; and sample 3 is a commercial sample from Leninabad Rare Metals Combine (Tajikistan).

interaction with water vapor in air. The hydrolysis reaction was performed at 40°C in a thermostated glass reactor equipped with a magnetic stirrer at a stirring rate of 800 rpm. A 10-ml portion of distilled water was added to a 0.0465-g portion of sodium borohydride placed in the reactor. Next, a catalyst was added to the reactor; the catalyst amount was calculated to obtain a specified metal/hydride molar ratio. The reactor was sealed with a nozzle connected to a burette. The volume of liberated hydrogen was measured using a 100-ml burette. The qualitative analysis of the resulting gas was performed using a Kristall-2000 chromatograph (OAO IZhMZ Kupol). The normalized rate of hydrogen generation (r) was calculated using the equation

$$r = \frac{V_{H_2}}{t_{1/2}m},$$

where r is the rate of reaction ((ml H_2) g^{-1} s^{-1}); V_{H_2} is the volume of hydrogen (ml (NTP)) liberated in the half-reaction time $t_{1/2}$ (s); and m is the weight (g) of a catalyst or an active component (Rh, Pt, Pd, or Ru) of the catalyst.

The specific surface area (S_{BET}) was determined from the thermal desorption of argon; the relative determination error was ±10%.

The concentrations of impurities in TiO_2 were found using inductively coupled plasma atomic emission spectrometry on an Optima 4300 DV instrument (Germany). For the determination of sulfur, acid extracts from the samples in hydrochloric acid were taken. The analysis for Nb, Fe, and Ca was performed after dissolving a weighed portion of TiO_2 in H_2SO_4 with the addition of HF. The relative determination error was ±5%.

The diffraction patterns of samples were obtained on a URD-63 diffractometer (Germany) using CuK_α radiation. The sizes of coherent scattering regions (CSRs) were calculated using the Scherrer equation based on the halfwidths of the strongest diffraction peaks: (101) and (110) for anatase and rutile phases, respectively. The CSR size determination error was ~10%. At a low concentration of a particular phase (less than 4%), it was impossible to evaluate reliably the CSR size. The quantitative analysis of individual crystalline phases in the samples was performed with the use of the PCW program.

The UV–vis diffuse reflectance spectra were measured in air at room temperature using a Specord M-40 spectrometer (Carl Zeiss Jena) with a standard diffuse-reflectance attachment. The absorption of a support was compensated for in the measurement of the spectra. In the analysis of unreduced catalysts, a parent support sample was used for compensation, whereas a support sample treated with $NaBH_4$ was used in the analysis of catalysts reduced with sodium borohydride.

RESULTS AND DISCUSSION

The hydrolysis of sodium borohydride begins even at room temperature, and the rate of hydrogen generation increases with temperature. The complete conversion of $NaBH_4$ cannot be reached because of an increase in the pH of the solution [10]. In the presence of the nanodispersed powders of platinum group metals, the rate of hydrogen generation increases dramatically. However, the catalytic activity of metals is irreproducible from experiment to experiment, and it varies over a wide range (20–30%) [11]. Dragieva et al. [12] related this instability to changes in the size of metal particles over a wide range and to the subsequent parti-

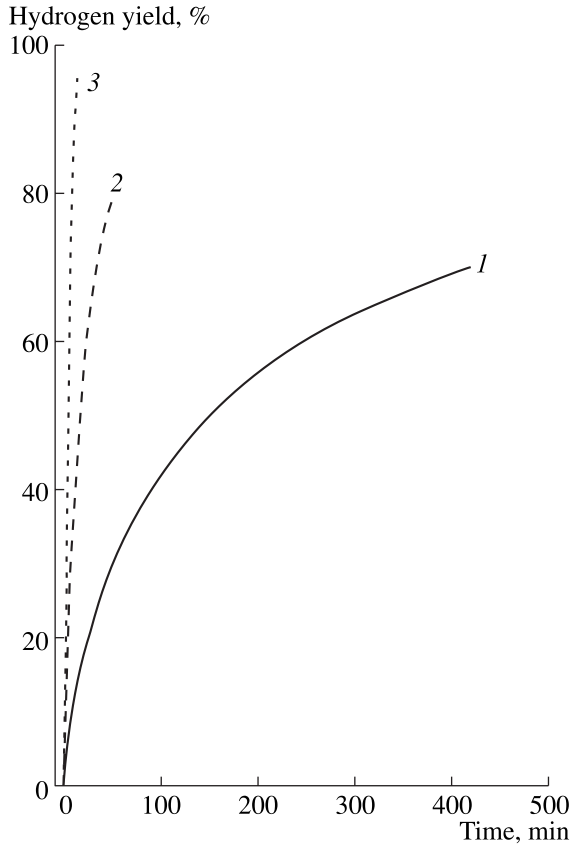

Fig. 1. Hydrogen generation at 40°C (*1*) in the absence of a catalyst and in the presence of (*2*) a bulk rhodium catalyst and (*3*) a supported Rh/TiO_2-**1** catalyst. The $Rh/NaBH_4$ molar ratio is 1 : 2000.

cle agglomeration in the course of the hydrolysis of $NaBH_4$.

The results of this work are indicative of the advantages of supported catalysts used for the hydrolysis of $NaBH_4$ over monometallic powders. It can be seen in Fig. 1 that the rate of hydrolysis of sodium borohydride in the absence of a catalyst gradually decreased with time; and the yield of hydrogen was 70% in 420 min. The addition of nanodispersed rhodium powder, which was prepared by the reduction of rhodium chloride in a medium of sodium borohydride, allowed us to increase the rate of hydrogen generation: a 70% yield was reached even in 33 min. Only 6 min was required for reaching the same conversion on the Rh/TiO_2-**1** catalyst. Moreover, the presence of a supported catalyst allowed us to reach a maximum yield of hydrogen. Thus, we can conclude that the supporting of a metal onto the surface of a carrier stabilizes rhodium nanoparticles and increases their activity. Figure 2 shows an electron micrograph of supported rhodium particles formed in a medium of sodium borohydride. These particles are characterized by a narrow size distribution over the range 2–3 nm.

Table 2. Rates of hydrogen release ((ml H_2) g^{-1} s^{-1}, normalized to 1 g of a catalyst) from aqueous $NaBH_4$ solutions at 40°C and a stirring rate of 800 rpm

Support	Active component			
	Rh	Pt	Ru	Pd
γ-Al_2O_3	4.5	2.3	–	–
Sibunit	10.8	7.3	7.0	0.8
TiO_2-1	30.3	14.3	16.1	2.0

Note: The metal/$NaBH_4$ ratio was 1 : 2000 for Rh, Pt, and Ru catalysts; the Pd/$NaBH_4$ ratio was 1 : 1000 for a Pd catalyst.

As can be seen in Table 2, the activity of Pt, Rh, Ru, and Pd metals supported onto Sibunit, γ-Al_2O_3, and TiO_2 (anatase) decreases in the order Rh > Pt ≈ Ru ≫ Pd. This relation is obeyed with the use of all three test supports. The order found in this work is somewhat different from that obtained by Prokopchik et al. [11, 13–15]; in these publications, the activity of bulk systems in the reaction of $NaBH_4$ hydrolysis decreased in the order Rh > Pt > Pd > Ru. It is also different from the order Pt > Rh > Ru ≈ Pd, which was published by Kojima et al. [4] and obtained with the use of titanium dioxide as a support. This is likely due to differences in catalyst preparation procedures.

The rate of hydrogen release in the presence of Pd-containing catalysts is low. As exemplified by the Pd/C catalyst (henceforth, the symbol C refers to Sibunit), it can be seen (Fig. 3) that it rapidly loses its activity and the rate of generation approaches the level of sodium borohydride decomposition in the absence of a catalyst. With consideration for the well-known ability of palladium to absorb considerable amounts of hydrogen [16], it is believed that catalyst deactivation is due to hydrogen adsorption on palladium with the formation of the strong Pd–H bond[1] [17].

In addition, the nature of not only an active component but also a support affects the activity of supported catalysts. A comparison between the rates of hydrogen release per gram of rhodium with the use of various supports (Fig. 4) shows that the activity of catalysts supported on Sibunit and γ-Al_2O_3 differs only slightly from the activity of bulk rhodium, which was prepared by the reduction of rhodium chloride with a solution of sodium borohydride. Moreover, the rate of hydrogen release on Rh/γ-Al_2O_3 was even lower than that on the bulk catalyst. To reveal the reason for this low activity, we studied the electronic state of rhodium on the surface of aluminum oxide using UV–vis diffuse reflectance spectroscopy.

Figure 5 shows the UV–vis diffuse reflectance spectra of a mechanical mixture of MgO and rhodium chlo-

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[1] The Pd–H bond energy is 240 kJ/(mol Pd) at the surface coverage $\theta = 0.5$ [18].

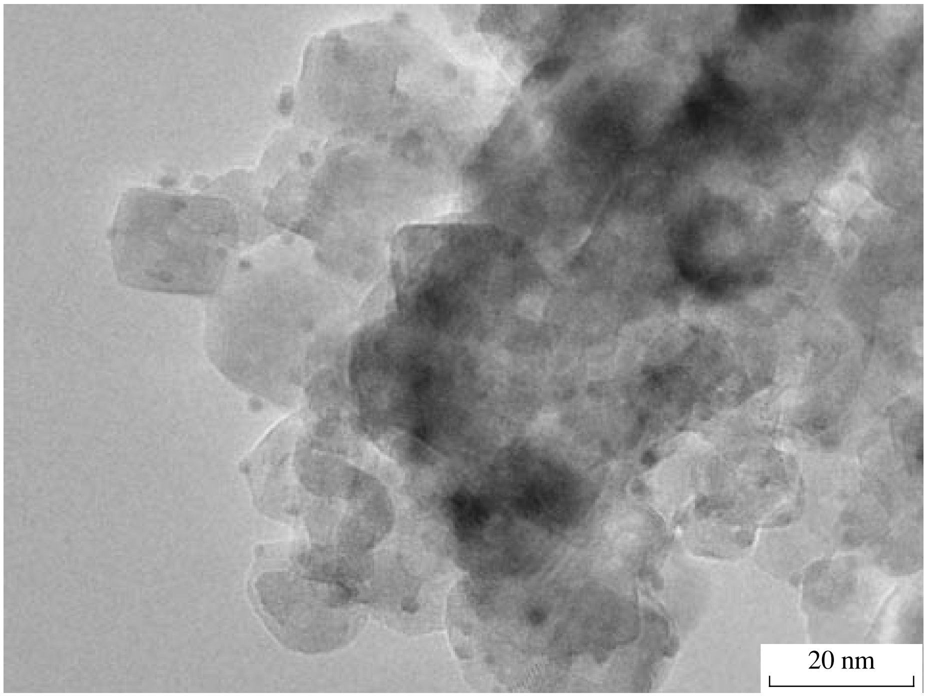

Fig. 2. Electron micrograph of the surface of an Rh/TiO_2 catalyst.

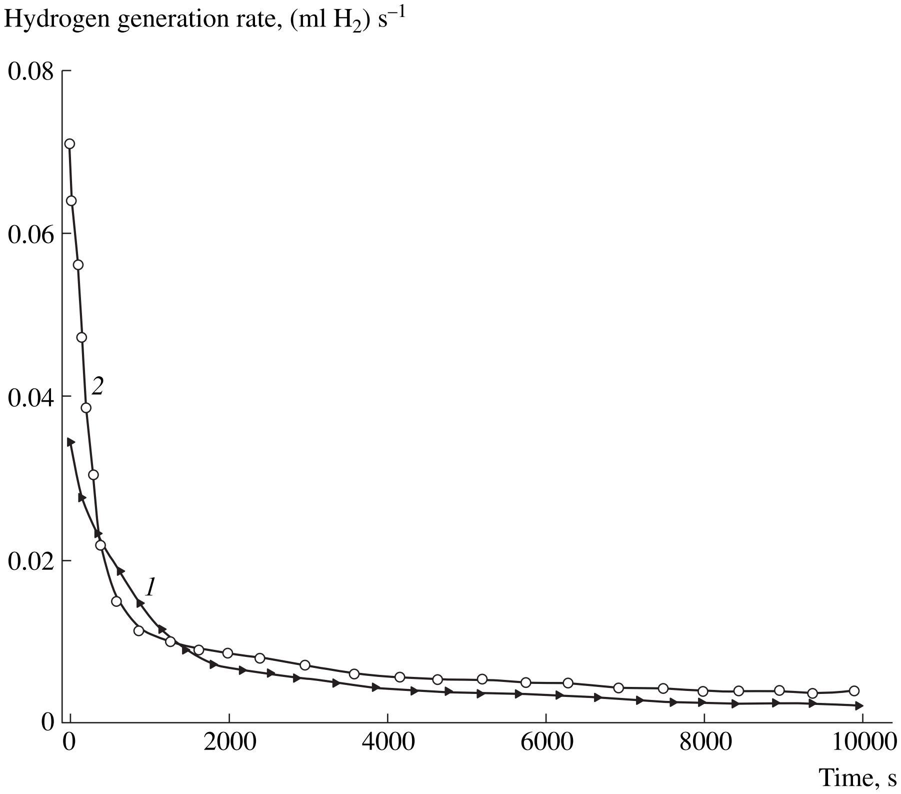

Fig. 3. Dependence of the rate of hydrogen release from aqueous $NaBH_4$ solutions on reaction time at 40°C: (*1*) in the absence of a catalyst and (*2*) in the presence of Pd/C. The $Pd/NaBH_4$ molar ratio is 1 : 1000.

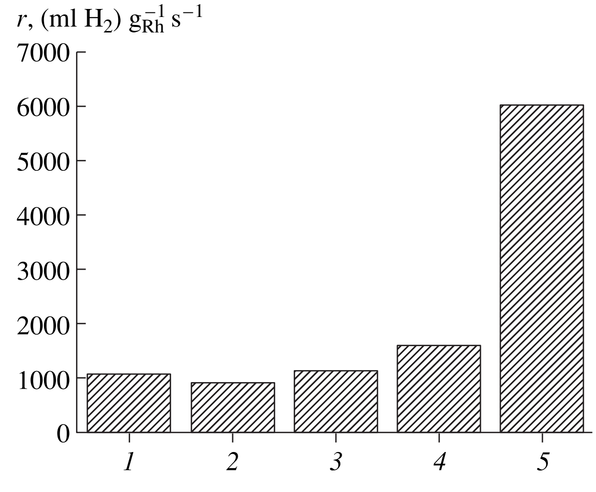

Fig. 4. Rate of hydrogen release (normalized to 1 g of rhodium) from aqueous $NaBH_4$ solutions at 40°C in the presence of Rh-containing catalysts: (*1*) bulk Rh, (*2*) Rh/γ-Al_2O_3, (*3*) Rh/C, (*4*) bulk Rh with the addition of a weighed portion of TiO_2 in the course of the reaction, and (*5*) Rh/TiO_2-**1**. The Rh/$NaBH_4$ molar ratio is 1 : 2000.

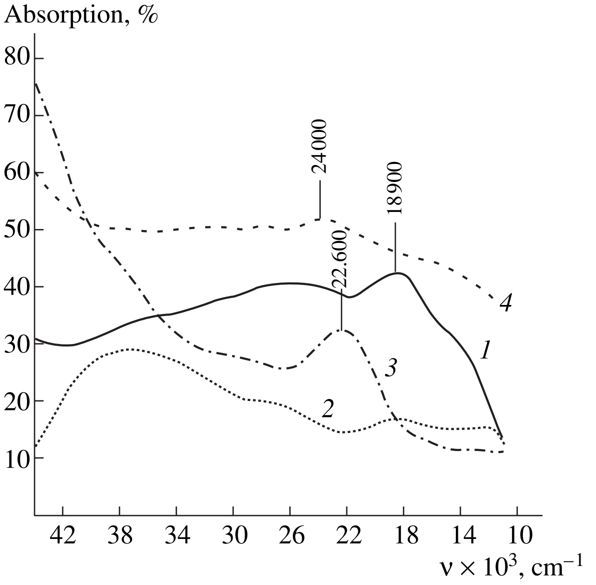

Fig. 5. UV–vis diffuse reflectance spectra: (*1*) a mechanical mixture of MgO with $RhCl_3 \cdot nH_2O$, (*2*) γ-Al_2O_3, (*3*) unreduced Rh/γ-Al_2O_3, and (*4*) reduced Rh/γ-Al_2O_3.

ride (spectrum *1*), parent aluminum oxide (spectrum *2*), unreduced Rh/γ-Al_2O_3 (spectrum *3*), and Rh/γ-Al_2O_3 reduced with sodium borohydride (spectrum *4*). As can be seen, these spectra differ noticeably from each other. The spectrum of the parent salt (*1*) exhibited absorption bands in the region 28000–11000 cm^{-1}. According to Lever [19], these absorption bands can be attributed to *d–d* transitions in the hexacoordinated Rh^{3+} ion. An absorption band at 18900 cm^{-1} was the most intense of these bands. Upon supporting $RhCl_3$ onto the surface of aluminum oxide, the position of this absorption band shifted by 3700 cm^{-1} to the high-frequency region (spectrum *3*; absorption band at 22600 cm^{-1}). Along with changes related to *d–d* transitions, a prominent high-frequency shift of the charge-transfer band and an increase in the intensity of this band were also observed. Thus, the electronic states of bulk and supported rhodium chloride differ significantly. This is likely due to the strong interaction of the parent rhodium salt with the surface of aluminum oxide up to the formation of a new surface compound [20].

After the reduction of the Rh/γ-Al_2O_3 catalyst under the action of a reaction medium (sodium borohydride), structureless absorption was observed in the region 28000–11000 cm^{-1} (Fig. 5, spectrum *4*), which suggests the formation of rhodium metal. However, an absorption band at 24000 cm^{-1} and absorption above 42000 cm^{-1}, which suggest the presence of Rh^{3+} ions, were observed against the background of nonselective absorption. It is likely that the presence of rhodium ions in the reduced sample can be explained by either the stabilization of an oxidized state of rhodium in the resulting surface compound and the incomplete reduction of it or the rapid reoxidation of rhodium metal in air [21]. It is believed that the occurrence of a portion of rhodium in an oxidized state on the surface of Rh/γ-Al_2O_3 is responsible for its lowest activity.

As can be seen in Table 2, a rhodium catalyst prepared based on titanium dioxide exhibited the maximum activity. The rate of hydrogen generation on this catalyst (Fig. 4) was higher than that on bulk rhodium by a factor of more than 5. The addition of a weighed portion of titanium dioxide to a reaction medium containing an aqueous solution of rhodium chloride and sodium borohydride allowed us to increase the rate of hydrogen release by 30% (Fig. 4). It is likely that rhodium metal particles, which were formed in solution in the course of rhodium chloride reduction, were adsorbed on the surface of titanium dioxide to produce centers that are more active in the hydrolysis of sodium borohydride. The high reactivity of rhodium on the surface of titanium dioxide is related to the formation and stabilization of supported nanodispersed rhodium metal particles in a medium of sodium borohydride (Fig. 2) and, probably, changes in the electronic properties of metal clusters because of their interaction with the support. The effect of the strong interaction of rhodium with titanium dioxide in catalysts reduced with hydrogen at high temperatures is well known [22].

A comparative study of rhodium catalysts (Fig. 6) prepared based on commercial titanium dioxide samples demonstrated that they exhibited lower activity than that of a catalyst based on TiO_2-**1** from Sigma-Aldrich. The differences were likely due to lower specific surface areas and the presence of impurities in commercial samples (Table 1). The rate of hydrogen generation in the presence of the Rh/TiO_2-**3** catalyst was much lower than that in the presence of Rh/TiO_2-**2**, although

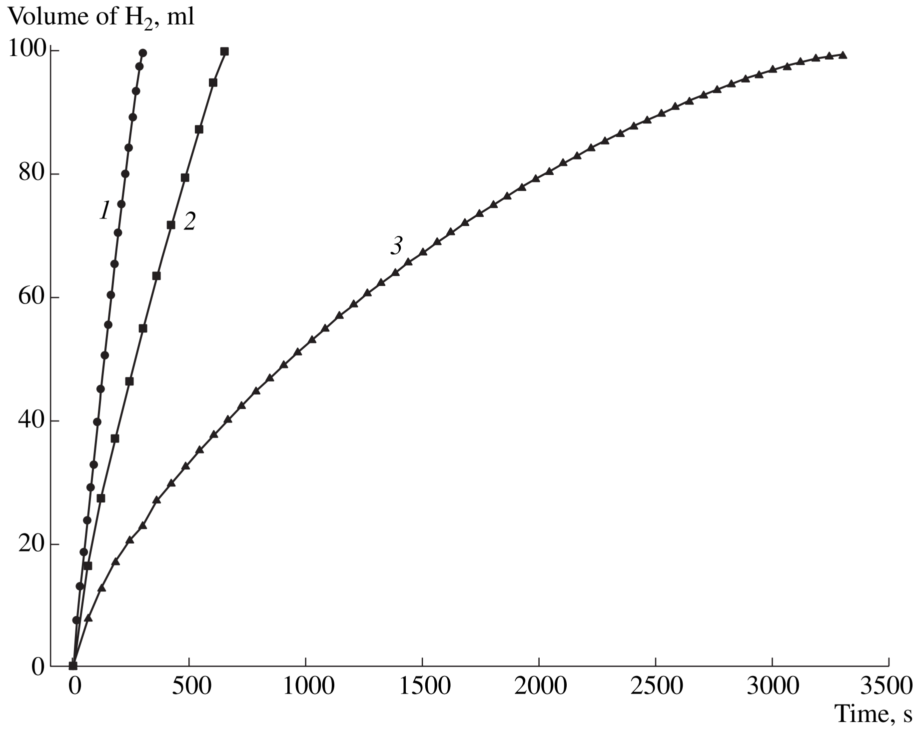

Fig. 6. Hydrogen generation at 40°C in the presence of supported Rh catalysts: (*1*) Rh/TiO_2-**1**, (*2*) Rh/TiO_2-**2**, and (*3*) Rh/TiO_2-**3**. The Rh/$NaBH_4$ molar ratio is 1 : 2000.

the texture characteristics of TiO_2-**2** and TiO_2-**3** were similar. It is believed that the occurrence of sufficiently strong Brønsted acid sites [23] on the surface of sulfate-containing TiO_2-**3** (Table 1) affects the electronic state of rhodium metal clusters [24, 25], and this decreases the activity of Rh/TiO_2-**3** in the test reaction.

To study the effect of the surface chemistry of anatase titanium dioxide on the state of rhodium chloride, we analyzed the UV–vis diffuse reflectance spectra (Fig. 7) of rhodium chloride supported onto TiO_2-**2** (spectrum *1*) and sulfate-containing TiO_2-**3** (spectrum *2*) and the spectrum of a mechanical mixture of MgO and $RhCl_3$ (spectrum *3*). Spectra *1–3* differ noticeably from one another. Let us analyze them in more detail. Initially, we compare the spectra of Rh/TiO_2-**2** and Rh/TiO_2-**3** samples (*1* and *2*, respectively) with the spectrum of a mechanical mixture of MgO and $RhCl_3$ (*3*). It is believed that the interaction between the components of this mixture is insignificant. The spectra of all of the test samples exhibit three absorption bands in the region 28000–11000 cm^{-1}. According to Lever [19], these absorption bands can be attributed to *d–d* transitions in the hexacoordinated Rh^{3+} ion. However, unlike the spectrum of the mechanical mixture of MgO and $RhCl_3$, absorption bands due to the *d–d* transitions are better resolved in the UV–vis diffuse reflectance spectra of the supported samples. Evidently, this is due to a decrease in the effect of charge transfer on the *d–d* transitions in the Rh^{3+} ion because of an increase in the degree of dispersity of the parent salt after supporting it onto the carrier surface. Taking into account this circumstance, we can perform a more detailed analysis of spectral curves. The intensity of an absorption band at 25000 cm^{-1} in the UV–vis diffuse reflectance spectrum of the Rh/TiO_2-**2** sample (spectrum *1*) is much higher than the intensity of a similar absorption band at 24800 cm^{-1} in the spectrum of the Rh/TiO_2-**3** sample (*2*). In this case, an absorption band at 20000 cm^{-1} in the spectrum of Rh/TiO_2-**3** exhibits a lower intensity and it is somewhat broadened and shifted by 500 cm^{-1} to the high-frequency region with reference to an analogous absorption band in the spectrum of Rh/TiO_2-**2**. Note that the absorption band at 24800 cm^{-1} in the spectrum of the Rh/TiO_2-**3** sample can be related to *d–d* transitions in the Rh^{3+} ion with a certain degree of probability, whereas the intense absorption band at 25000 cm^{-1} in the spectrum of Rh/TiO_2-**2** cannot be related to only this transition.

Previously, a similar absorption band was observed in a study of the interaction of vanadium and copper compounds with the surface of titanium dioxide. Its appearance was related to the formation of a Ti–O–metal bond. According to published data [26, 27], absorption in the region of the spectrum under consideration characterizes the degree of interaction of a metal with the surface of the support (TiO_2). In this case, the higher the absorption band intensity at 25000 cm^{-1}, the higher the concentration of metal ions that form the above bond. The presence of sulfate ions on the surface of TiO_2 significantly decreases the inten-

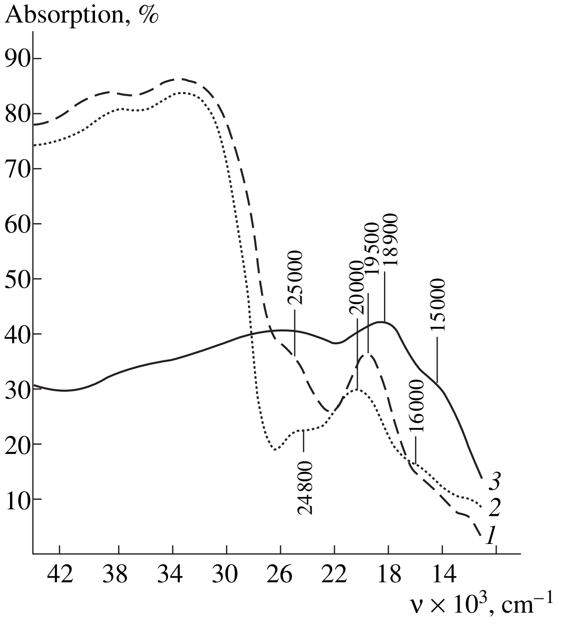

Fig. 7. UV–vis diffuse reflectance spectra of the samples: (*1*) Rh/TiO_2-**2**, (*2*) Rh/TiO_2-**3**, and (*3*) a mechanical mixture of MgO with $RhCl_3 \cdot nH_2O$.

sity of this absorption band because of the interaction of the metal with sulfate groups [28].

We believe that, upon supporting rhodium chloride, it interacts with the surface of TiO_2-**2**. If a rhodium salt is supported onto sulfate-containing titanium dioxide TiO_2-**3**, it interacts with sulfate ions. This hypothesis is supported by a gradual shift of the most intense absorption band at 18900 cm^{-1} in the spectrum of the parent salt after supporting it onto the surface of the test samples of titanium dioxide. The shift of this absorption band to the high-frequency region, which is indicative of an increase in the ligand field, suggests a change in the state of the first coordination sphere of the rhodium ion. It is likely that the increase in the ligand field was due to the replacement of one or more ligands in the parent $RhCl_3$ salt by the surface oxygen of the TiO_2-**2** support or the SO_4^{2-} group of the TiO_2-**3** support. The observed differences in the UV–vis diffuse reflectance spectra of the samples prepared based on TiO_2-**2** and sulfate-containing TiO_2-**3** are indicative of different compositions and structures of the resulting surface complexes. It is likely that this is responsible for the further ability of the above complexes to undergo reduction in a medium of sodium borohydride and the reactivity of the resulting rhodium metal complexes in the reaction of sodium borohydride hydrolysis.

The development of hydrogen generators for fuel cells with the use of the hydrolysis of sodium borohydride requires a detailed study of the reaction in the presence of catalysts. The results obtained in this work indicate that the nature of the support and the active component of the catalyst affects the rate of hydrogen generation. We found that the activity of catalysts on all three test supports decreases in the order Rh > Pt ≈ Ru ≫ Pd. It is likely that the lowest reactivity of a palladium catalyst is due to the formation of a strong Pd–H bond. Of rhodium catalysts based on Sibunit, γ-Al_2O_3, and TiO_2, Rh/TiO_2 exhibits the highest activity. It is likely that the difference in the reactivity of rhodium catalytic systems is related to the interaction of the precursor of an active component with the support. According to UV–vis diffuse reflectance spectra, complexes of the precursor of an active component with the support are formed in the course of supporting rhodium chloride. Differences in the composition and structure of surface complexes depend on the nature of the support. The further reduction of these complexes in a reaction medium of sodium borohydride results in the formation of metal clusters, which exhibit various reaction properties.

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