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Activity of Rh/TiO₂ Catalysts in NaBH₄ Hydrolysis: The Effect of the Interaction between RhCl₃ and the Anatase Surface during Heat Treatment

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Abstract—The reaction properties of Rh/TiO₂ sodium tetrahydroborate hydrolysis catalysts reduced directly in the reaction medium depend on the temperature at which they were calcined. Raising the calcination temperature to 300° C enhances the activity of the Rh/TiO₂ catalysts. Using diffuse reflectance electronic spectroscopy, photoacoustic IR spectroscopy, and chemical and thermal analyses, it is demonstrated that, as RhCl₃ is supported on TiO₂ (anatase), the active-component precursor interacts strongly with the support surface. The degree of this interaction increases as the calcination temperature is raised. TEM, EXAFS, and XANES data have demonstrated that the composition and structure of the rhodium complexes that form on the titanium dioxide surface during different heat treatments later determine the state of the supported rhodium particles forming in the sodium tetrahydroborate reaction medium.

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The necessity of developing and commercializing safe and reliable power sources with a long service life has initiated R&D activities in the field of fuel-cell power plants. The functioning of a fuel cell is impossible without a hydrogen generation and storage system. The catalytic hydrolysis of NaBH₄ is viewed as a promising means of generating high-purity hydrogen for portable power sources [1, 2].

Researchers are now making an intensive search for active and stable catalysts for sodium tetrahydroborate hydrolysis. In recent publications, there has been information concerning the high activity of supported platinum-metal (Pt, Ru, Rh) catalysts [3–8]. Unfortunately, relevant data are sparse and the state of the active component and catalyst synthesis methods have attracted researchers' attention only recently [9].

The preparation of supported-metal NaBH₄ hydrolysis catalysts by the impregnation method consists of two steps, namely, the interaction between the activecomponent precursor and the support surface and subsequent reduction. The catalyst reduction step is usually carried out directly in the NaBH₄ medium since sodium tetrahydroborate is a strong reducing agent even at room temperature [10]. Therefore, the catalyst preparation methods should allow the properties of the catalyst to be controlled at the precursor supporting stage [9]. The chemistry of the support surface plays a significant role in the catalytic action of supported rhodium catalysts [9]. It was assumed that it is the composition and structure of the active-component precursor that determine the reaction properties of the rhodium particles forming under the action of the reaction medium.

Here, we will report the state of anatase-supported rhodium chloride studied as a function of the thermal pretreatment temperature by a variety of physicochemical methods. We will also address the effect of heat treatment on the reactivity of the supported rhodium particles forming in the NaBH₄ hydrolysis medium.

EXPERIMENTAL

Catalyst Preparation

The support material for Rh/TiO₂ catalysts was TiO₂ powder (OOO Solikamskii Magnievyi Zavod) calcined at 500°C for 4 h. The specific surface area of the calcined sample was 74 m²/g. According to x-ray diffraction data, the main crystalline phase of the support was anatase (96%), which contained 4% rutile. The size of the coherent-scattering domain (CSD) in the [101] direction of anatase was 140 Å. Chemical analysis revealed the following impurities (wt %): Nb, 0.04; S, 0.03; Fe, 0.22; Ca, 0.58.

A series of Rh/TiO₂ catalysts was prepared by the incipient-wetness impregnation of titanium dioxide with an aqueous solution of RhCl₃ (OOO AURAT). The impregnated catalysts were dried in air at 50–60°C under an IR lamp and then at 110–130°C for 2 h. Next, the catalysts were additionally calcined at 300°C in air for 4 h. The rhodium content was varied between 1 and 6 wt %.

Physicochemical Methods

The Nb, Fe, and Ca contents of TiO_2 were determined by atomic emission spectroscopy with inductively coupled plasma on an Optima 4300DV spectrometer (PerkinElmer) after dissolving a titania sample in an appropriate mixture of acids. Sulfur was quantified in a hydrochloric acid extract from the sample.

The Rh and Cl contents of catalysts were determined by X-ray fluorescence analysis using a VRA-30 spectrometer with a Cr-anode X-ray tube.

The phase analysis of titanium dioxide was carried out on a URD-63 diffractometer (Freiberger Präzisionsmechanik) using CuK_{α} radiation. The CSD size was calculated using the Scherrer formula. Crystalline phases in the titanium dioxide sample were quantified using the PCW program [11].

Diffuse reflectance electronic spectra were recorded in air at room temperature on a Specord M-40 spectrophotometer (Carl Zeiss Jena) equipped with a standard diffuse reflectance attachment. The absorbance of the support was compensated when recording the spectra.

Photoacoustic IR spectra were recorded on an MB-102 Fourier transform spectrometer (Bomem) with an MTEC Model 300 photoacoustic attachment.

Electron micrographs were obtained using a JEM-2010 electron microscope (JEOL) with an accelerating voltage of 200 kV and a resolving power of 1.4 Å. Periodic patterns of the crystal structure were analyzed by numerical Fourier transform methods. After NaBH₄ hydrolysis, catalyst samples were isolated from the reaction medium, washed with distilled water, dried in air at 110–130°C, and placed on a holey copper substrate.

EXAFS spectra were recorded at the EXAFS station of the Siberian synchrotron radiation center. The spectra were obtained using a VEPP-3 booster at an electron energy of 2 GeV and an electron current of 110 mA in the transmission mode. The spectrometer had a Si(111) cut-off monochromator and proportional chambers as detectors. Rhodium *K*-edge absorption spectra were recorded in 2-eV steps. EXAFS data were processed by a standard procedure, using the VIPER program [12] to separate the oscillating component of the absorption coefficient and the FEFF-7 program [13] to calculate modeling parameters. XANES spectra were recorded using the same procedure, but with 0.4-eV energy steps. The catalysts were characterized both before and after NaBH₄ hydrolysis.

Thermal analysis was carried out in flowing air (25 l/h) in the temperature range 25–1000°C at a heating rate of 10 K/min on 200-mg samples (Q 1500 D thermoanalytical system). Heat-induced transformations in the sample were monitored by recording TG and DTG profiles.

The specific surface area was determined from argon thermal desorption data.





Fig. 1. Rate of hydrogen evolution from aqueous NaBH₄ solutions as a function of the rhodium content of the catalysts heat-treated in air at (1) 110–130 and (2) 300°C.

Testing of Catalysts in NaBH₄ Hydrolysis

The hydrogen generation process was studied for sodium tetrahydroborate (98%, Sigma-Aldrich) dissolved in distilled water. Hydrolysis was carried out at 40°C in a temperature-controlled glass reactor with a magnetic stirrer at a stirring speed of 800 rpm. Sodium tetrahydroborate (0.0465 g) was placed into the reactor, and distilled water (10 ml) was added. Next, a catalyst (6.2 mg) was added. The reactor was then sealed airtightly with a gas outlet adapter connected to a 100-ml burette. The normalized hydrogen generation rate (*w*) was determined as

$$w = \frac{V_{\mathrm{H}_2}}{t_{1/2}m},$$

where *w* is the reaction rate ((ml H₂) s⁻¹ (g Rh)⁻¹), V_{H_2} is the volume of hydrogen (ml NTP) released during the reactant half-life $t_{1/2}$ (s), and *m* is the weight of Rh (g) in the catalyst.

RESULTS AND DISCUSSION

Figure 1 plots the hydrogen generation rate per gram of Rh as a function of the rhodium content for Rh/TiO₂ catalysts subjected to different heat treatments. The specific activity of rhodium decreases as the metal content is increased from 1 to 6 wt %. Raising the calcination temperature to 300°C markedly enhances the specific activity of rhodium. This is particularly true for the catalysts containing >2 wt % Rh. Further raising the calcination temperature to 500°C has no significant effect on the catalytic activity. Thus, the change in the state of rhodium chloride on the titanium dioxide surface that is induced by raising the calcination tempera-

Thermal pretreatment temperature, °C	Rh content, wt %	Cl content, wt %	Rh : Cl molar ratio		
110–130	5.95	5.75	1:2.8		
300	5.94	4.44	1:2.2		
500	6.11	1.07	1:0.5		

Table 1. X-ray fluorescent analysis data for the unreduced (6 wt % Rh)/TiO₂ catalyst

ture from 110 to 300°C results in a substantial increase in the specific activity of supported rhodium reduced in the NaBH₄ reaction medium.

In order to study the interaction between rhodium chloride and the titanium dioxide surface, catalyst samples were examined by various physical methods and chemical analysis.

Table 1 lists chemical analysis data for the (6 wt % Rh/TiO_2) catalyst heat-treated in air at different temperatures. These data indicate that the chlorine content of this sample decreases starting at 300°C. Note that bulk rhodium chloride decomposes to turn into rhodium oxide at a higher temperature (Fig. 2). The lower decomposition temperature of supported rhodium chloride may be due to either its small particle size or its interaction with the titanium dioxide surface.

Diffuse reflectance data for supported rhodium chloride samples dried at 110–130°C and calcined at 300°C are presented in Fig. 3. According to earlier data [9, 14], the absorption band at 19600 cm⁻¹ is due to the d-d transition in a hexacoordinated Rh³⁺ complex. Absorption at 25000 cm⁻¹ was observed in earlier studies of the interaction of transition metal cations with the



Fig. 2. Thermoanalytical curves for the decomposition of $RhCl_3 \cdot nH_2O$ in air.

TiO₂ surface, and it was assigned to charge transfer from oxygen to the metal [9, 15, 16]. Apparently, the 25000 cm⁻¹ band observed in this study is also due to the interaction of Rh³⁺ complexes with the surface oxygen of anatase. An analysis of the diffuse reflectance curves suggests that raising the calcination temperature from 110–130 to 300°C results in an increase in the total absorbance in the diffuse reflectance spectra and in a marked strengthening of this charge-transfer band. Therefore, the electronic state of rhodium in the unreduced catalysts depends on the calcination temperature.

In order to understand the changes in the diffuse reflectance spectra caused by the heat treatment of the catalysts, we recorded the photoacoustic IR spectrum of supported rhodium chloride (1 wt % Rh) dried at 110–130°C and calcined at 300°C and the same spectrum of the initial titanium dioxide calcined under the same conditions (Fig. 4). Clearly, the calcination of the catalyst at 300°C causes a marked decrease in its water content. The water content of the calcined catalyst is



Fig. 3. Diffuse reflectance electronic spectra of the unreduced catalysts containing (1, 2) 1 and (3, 4) 6 wt % Rh: (1, 3) catalysts dried at 110–130°C; (2, 4) catalysts calcined at 300°C.

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Fig. 4. Photoacoustic IR spectra of (1) the initial TiO₂ calcined at 300°C, (2) the unreduced (1 wt % Rh)/TiO₂ catalyst dried at 110–130°C, and (3) the same catalyst calcined at 300°C.

not only below the water content of the catalyst dried at 110–130°C, but also below the water content of titanium dioxide calcined at 300°C. The decrease in absorbance in the 3350–2270 cm⁻¹ region suggests that both weakly and strongly bonded water is removed from the support surface at this temperature [17].

Thus, both the marked strengthening of the chargetransfer band at 25000 cm⁻¹, which characterizes the degree of interaction between rhodium and the titanium dioxide surface, and the growth of the total absorbance in the diffuse reflectance spectrum upon the calcination of the sample at 300°C are evidence that the chemical interaction between the rhodium complexes and the surface sites of TiO₂ is strengthened. This is accompanied by strengthening of the charge transfer effect on the *d*-*d* transitions. This is likely due to the increase in the degree of covalence of the metal-ligand bond, which arises from the partial replacement of chlorine atoms by oxygen atoms in the coordination sphere of Rh³⁺ and from the strengthening of the effect of the support on the state of the surface cluster.

Since, as was mentioned above, rhodium chloride calcined at 300°C contains a smaller amount of strongly bonded water than the support calcined under the same conditions, it is obvious that the most likely locations of the rhodium complex are the surface sites of titanium dioxide that were previously occupied by strongly bonded water molecules [18, 19].

According to TEM data, the degree of interaction between the supported salt and titanium dioxide has a considerable effect on the state of the rhodium particles that form in the reaction medium under the reductive action of sodium tetrahydroborate. Figure 5 shows images of catalysts (6 wt % Rh) that have been tested in NaBH₄ hydrolysis. As was noted above, it is at high





Fig. 5. Electron micrographs of the (6 wt % Rh)/TiO₂ catalyst reduced in the NaBH₄ reaction medium: (a) catalyst dried at 110–130°C; (b) catalyst calcined at 300°C.

rhodium contents that the catalytic activity increases significantly as the calcination temperature is raised (Fig. 1). It is clear from Fig. 5a that, in the (6 wt % Rh)/TiO₂ catalyst dried at 110–130°C, the titanium dioxide surface has metal particles of mean size 3.3 nm.

Table 2. Shift of the maximum of the first derivative of the *K*-edge absorbance of rhodium (ionization of the 1*s* level) according to XANES data

Sample	Shift, eV		
Rh foil	0		
RhCl ₃ /TiO ₂ (6 wt % Rh), 110–130°C	1.32		
RhCl ₃ /TiO ₂ (6 wt % Rh), 300°C	2.63		
Rh/TiO ₂ (6 wt % Rh), 110–130°C, reduced by $NaBH_4$	0		
Rh/TiO ₂ (6 wt % Rh), 300°C, reduced by NaBH ₄	1.91		
Rh ₂ O ₃	3.94		



Fig. 6. Experimental (solid lines) and calculated (dashed lines) atomic radial distribution functions for the (6 wt % Rh)/TiO₂ catalyst reduced in the NaBH₄ reaction medium after different heat treatments.

Raising the calcination temperature to 300°C decreases the mean size of the rhodium particles in the reduced sample to a slightly smaller value of 2.7 nm (Fig. 5b). In addition, the rhodium particles in this sample are completely or partially "decorated" with titanium dioxide. This is likely due to the strong interaction between the support and the active component.

In order to study the charge state of the rhodium particles reduced in the sodium tetrahydroborate medium, we measured the shifts of the maxima of the first derivative of K-edge absorbance of rhodium (ionization of the 1s level) by the XANES method (Table 2). The zero value was assigned to the shift observed for rhodium foil. An analysis of the XANES data suggests that the catalyst pretreatment temperature has an effect on the charge state of the rhodium particles reduced in the reaction medium, which were examined after NaBH₄ hydrolysis. If, in a sample that was simply dried before being reacted with the NaBH₄ solution, the charge state of the reduced rhodium particles is close to metallic, additional calcination at 300°C will not result in the complete reduction of rhodium, which will remain partially oxidized (according to the EXAFS data presented below, one-third of the introduced rhodium is in the oxidized state). It is also possible that the rhodium metal nanoparticles gain positive charge owing to the presence of Rh–O bonds on their surfaces.

Our EXAFS data confirm the presence of oxygen in the coordination environment of the Rh atoms in the reduced catalysts that have been tested in NaBH₄ hydrolysis. Figure 6 plots the atomic radial distribution functions, and Table 3 lists interatomic distances (R) and coordination numbers (N) for the nearest neighbors of the rhodium atoms. The first coordination sphere of rhodium in the catalyst sample that was dried at 110– 130°C before reduction has an interatomic distances are equal to Rh–Rh distances in rhodium metal. Calcination at 300°C reduces the coordination numbers corresponding to the Rh–Rh distances and increases the coordination number corresponding to the Rh–O distance.

Thus, for the reduced catalyst that was calcined at 300°C, which consists of metallic and oxide phases, EXAFS data indicate that rhodium is either in one charge state or in two similar charge states for which the absorption edge shift is smaller than is observed for Rh_2O_3 (Table 2). A plausible explanation of this fact is that the reduction of the catalyst actually yields one mixed rhodium phase in which a metal core is partially covered by an oxide phase or is fixed to it. If this is the case, the electronic state of the entire particle will be averaged out. This is indicated by the absence of Rh–

Table 3. EXAFS data for the (6 wt % Rh)/TiO₂ catalyst reduced in the NaBH₄ reaction medium

Treatment	Rh–O		Rh–Rh		Rh–Rh		Rh–Rh		Rh–Rh		ΔE_0 ,	R fac-
	<i>R</i> , Å	Ν	<i>R</i> , Å	N	eV	tor, %						
Heat treatment at 110°C	2.01	0.97	2.68	5.89	3.77	4.40	4.67	2.30	5.27	3.69	-0.11	18.98
Heat treatment at 300°C	2.02	2.06	2.68	4.68	3.88	0.14	4.67	1.06	5.27	1.04	-3.09	23.95
Rh metal	-	-	2.69	12	3.80	6	4.66	24	5.38	12	-	-

Rh distance peaks characteristic of Rh_2O_3 (2.99, 3.52, and 3.75 Å) [20] in the atomic radial distribution curve. The nonstoichiometric oxide will possess intrinsic conductivity, and the contact between the two conducting phases will result in the formation of a single Fermi level.

This change of the electronic properties of the metal particles that are in chemical contact with the conducting oxides provides a plausible explanation for the strong interaction effect well-known in the synthesis of metal catalysts supported on transition-metal oxides.

An analysis of these results together with data of other physicochemical methods suggests that the difference between the NaBH₄ hydrolysis activities of catalysts subjected to different heat treatments correlates with the appearance of a peak due to the Rh–O distance in the EXAFS spectra of the catalysts reduced in the reaction medium. This is likely explicable in terms of the composition and structure of the surface rhodium compounds that form at the impregnation and heat treatment stages of the supporting of rhodium chloride on the titanium dioxide surface.

CONCLUSIONS

This study has demonstrated that the conditions under which the active-component precursor being supported (rhodium chloride) interacts with the titanium dioxide surface are a significant factor in the NaBH₄ hydrolysis activity of the Rh/TiO₂ catalysts obtained by reduction directly in the reaction medium. Raising the heat-treatment temperature from 110–130 to 300°C for supported rhodium chloride enhances the activity of the Rh/TiO₂ catalysts. The growth of the specific catalytic activity of rhodium is most pronounced for the catalysts containing >2 wt % Rh. It has been demonstrated by a variety of physicochemical methods that, as RhCl₃ is supported on the anatase modification of TiO₂, the active-component precursor interacts strongly with the support surface. As the temperature is raised, the interaction between the surface complexes of rhodium and titanium dioxide strengthens. The Rh³⁺ complexes are likely located on surface sites that were previously occupied by adsorbed water molecules. The removal of water from the anatase surface at 300°C causes partial replacement of chlorine atoms in the first coordination sphere of Rh³⁺ by oxygen atoms from the TiO₂ surface. The state of supported rhodium chloride determines the state of the supported rhodium metal particles in the catalysts after their reduction during NaBH₄ hydrolysis. The calcination of supported rhodium chloride at 300°C reduces the mean diameter of reduced rhodium particles. These rhodium are completely or partially decorated with titanium dioxide. This is evidence of the strong interaction between the support and the active component. Furthermore, the interaction between supported rhodium chloride and anatase exerts an effect on the electronic properties of the reduced rhodium particles.

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