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Effect of the Distribution of Palladium over the Cross Section of an Ion-Exchanger Fiber on Catalyst Activity in a Water Deoxygenation Process

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Abstract—A procedure for the preparation of a fibrous palladium-containing catalyst for the removal of dissolved oxygen from water was developed. This procedure includes the preliminary modification of an anion-exchanger fiber with carboxylate ions, which makes it possible to localize metal clusters in a thin subsurface layer of a fiber at the subsequent stages of the ion-exchange introduction of palladium into the carrier and the reduction of palladium. It was found that the higher activity of fibrous palladium-containing catalysts based on the citrate forms of anion exchangers, as compared with that of samples based on the chloride forms, was due to the predominant arrangement of reduced metal clusters on the external surface and an adjacent thin layer of the fiber.

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INTRODUCTION

In recent years, the catalytic removal of dissolved oxygen from water based on the reduction of oxygen with hydrogen with the formation of water came to the increasing attention of researchers [1–10].

Deoxygenated water is used in power engineering, microelectronics, chemical industry, and food industry. A large number of catalytic installations for water deoxygenation with the use of Lewatit granulated palladium-containing catalysts are currently in operation in economically developed countries [1–3]. The catalytic deoxygenation of water is an ecologically clean process because it does not require additional chemical reagents. It is performed over a sufficiently wide range of temperatures (from 0 to 40°C). This process does not require the removal of salts from purified water, and it is characterized by lower (by 60–70%) capital and operational expenditures in comparison with the energy-consuming processes of thermal or vacuum deaeration.

We synthesized and studied palladium-containing catalysts [11] based on fibrous anion exchangers with a gel structure (unlike foreign catalysts based on granulated anion exchangers with a macroporous structure).

The fibrous form of an ion exchanger has certain advantages over the granulated form because the fiber diameter is smaller than the diameter of a granule by an order of magnitude. This results in a shortening of the diffusion path and, as a consequence, in the intensification of mass-exchange processes.

Catalysts with different arrangements of a metallic phase over the cross section of a granule or fiber can be synthesized using appropriate procedures [12]. An optimum depth of supporting an active constituent mainly depends on the value of ψ, the ratio of the rate of reaction to the rate of diffusion. At low values of ψ (<0.5), when the reaction occurs in the kinetic region, it is reasonable to uniformly support the active constituent or to arrange it at the central section. The effect of an increase in the concentration of the active constituent in the outer layers of a granule or fiber (the arrangement of a metal phase as a crust) comes into play at $\psi > 10$, that is, on condition that the reaction occurs at a high rate.

The interaction of oxygen and hydrogen dissolved in water is a diffusion-controlled reaction, and metal-containing "skin"-type catalysts are effective for this reaction [13].

Here, we propose a method for the localization of a metal (palladium) phase in a very thin subsurface layer of a fiber. The aim of this work was to obtain experimental data on the effect of a metal distribution over the cross section of a fiber on the activity of the Pd/anion exchanger catalyst in the process of water deoxygenation.

EXPERIMENTAL

The following idea formed the basis of catalyst preparation with the localization of palladium in a thin

Table 1. Main physicochemical characteristics of fibrous anion exchangers

Anion exchanger	Functional groups	Exchange capacity, mg-equiv/g	Fiber diameter, μm	Swelling, $g_{H_2O}/g_{\text{ion exchanger}}$
FIBAN A-5		4.43	40	1.31
	—COOH	0.33		
FIBAN A-6		1.96	40	1.66
		1.27		

subsurface layer of a fiber. Counterions (Cl^-) in the initial chloride form of a FIBAN A-5 or FIBAN A-6 anion exchanger are exchanged for the anions of an organic acid (which are bulkier and less mobile than Cl^- ions) to a maximally possible depth. After washing off the physically sorbed acid, the ion exchanger is brought into short-term contact with an acidified solution of palladium chloride (H_2PdCl_4). It is assumed that, in this case, the $PdCl_4^{2-}$ anions are exchanged for the organic acid anions only in a thin subsurface layer of the fiber. This assumption is based on the fact that the amount of functional groups in the ion exchanger is much greater than the amount of $PdCl_4^{2-}$ anions in the contacting solution (the palladium content of the catalysts was 0.15% on a support weight basis). Even at a limited exchange time, the almost complete absorption of palladium by the ion exchanger will occur in this case and the exchange migration of $PdCl_4^{2-}$ anions into the fiber will be dramatically decreased because of the large sizes of organic acid anions.

Table 1 summarizes the main physicochemical characteristics of FIBAN A-5 and FIBAN A-6 fibrous anion exchangers, which were used as supports for the preparation of catalysts. The FIBAN A-5 anion exchanger, which was synthesized based on Nitron D polyacrylic fiber by the amination of nitrile groups with *N*,*N*-dimethylaminopropylamine, contains weakly basic tertiary amino groups and a small amount of carboxyl groups, which were formed as a result of a side reaction of hydrolysis [14]. The FIBAN A-6 anion exchanger was prepared by the alkylation of FIBAN A-5 with epichlorohydrin, in the course of which the major portion (~60%) of weakly basic (tertiary) amino groups was converted into strongly basic quaternary amino groups.

The following carboxylic acids with different chemical structures, anionic sizes, and dissociation constants were used for the modification of anion exchangers: butyric, oxalic, succinic, tartaric, and citric acids. The carboxylate forms of a support were obtained by passing 0.1 M aqueous solutions of the carboxylic acids at a flow rate of 5 ml/min through a column with the swollen anion exchanger in the chloride form until a negative reaction for Cl^- ions. Then, the ion exchanger was washed with distilled water to a neutral reaction using methyl orange (pH 4.0–4.4).

Palladium was introduced into the chloride and carboxylate forms of anion exchangers by ion exchange. For this purpose, a fibrous support sample, which was swollen in water and wrung out, was rapidly immersed in a hydrochloric acid solution of palladium chloride (palladium concentration of 20 mg/l), exposed for 2 min, removed from the solution, and washed with distilled water for the removal of the acid. The degree of exchange was determined from the residual concentration of palladium in the solution.

Palladium-containing solutions were analyzed using a Vista Pro inductively coupled plasma atomic-emission spectrometer from Varian.

The samples containing $PdCl_4^{2-}$ ions were reduced with a 3% solution of formic acid (30 ml/g catalyst) at 40°C for 2 h. The prepared catalyst was washed with distilled water until a neutral reaction using methyl orange.

Ion-exchange palladium was extracted from the catalyst samples using an acidified solution of thiocarbamide [15]. The $PdCl_4^{2-}$ ions interact with thiocarbamide to form the water-soluble colored compound $[Pd(NH_2CSNH_2)_4]Cl_2$, which is stable at pH 0.2–1.6.

A weighed portion (0.2 g) of an air-dry unreduced sample was immersed in distilled water and kept for

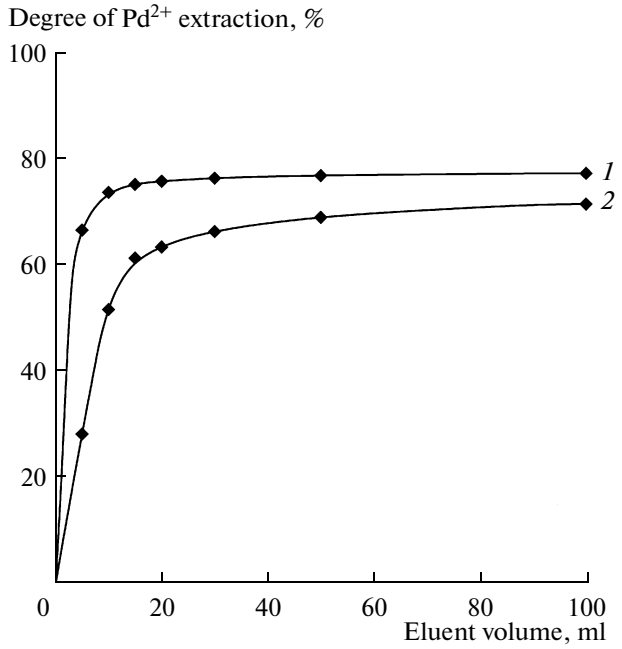


Fig. 1. Degree of Pd^{2+} extraction from unreduced catalyst samples based on FIBAN A-5 and FIBAN A-6 anion exchangers in the chloride form as a function of the volume of passed eluent: (*1*) 0.15% Pd/FIBAN A-6 and (*2*) 0.15% Pd/FIBAN A-5.

2 h to convert it into a swollen state. Then, the swollen sample was placed in a column (d_{int} = 7 mm), and 100 ml of a hydrochloric acid solution of thiocarbamide (a 0.1 M solution of NH_2CSNH_2 in a 0.1 M solution of HCl) was passed through it at a flow rate of 1.35 ml/min. Eluate samples corresponding to the specified volumes of the passed eluent were taken and analyzed for palladium. The degree of palladium extraction was calculated as the percentage ratio of the palladium content of the eluate at a specified volume of the passed eluent to the amount of palladium introduced into the ion exchanger by ion exchange.

The elemental composition of catalysts was studied using an INCA Energy 350 X-ray microanalysis system from Oxford Instruments (United Kingdom). The analyzer is an energy-dispersive spectrometer with a thermocycled high energy resolution detector, which is mounted as an attachment to a scanning electron microscope (in this case, a Mira instrument from Tescan, (Czech Republic) was used). Catalyst samples with an increased palladium content (1.0%) were prepared for analysis in accordance with the requirements of an operational procedure. The prepared samples were placed in a chamber of the scanning electron microscope, and the measurement was performed at an accelerating voltage of 20 kV. The working distance (WD), that is, a distance from the sample to the final lens, was 15 mm. The diameter of a detecting electron beam was about 0.5 μm.

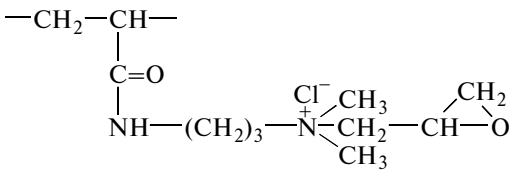
The activity of the catalysts was determined at a pilot plant for the catalytic deoxygenation of water [11].

RESULTS AND DISCUSSION

The degree of exchange of the counterions in the initial and modified support samples for $PdCl_4^{2-}$ anions was 99.8–99.9%.

Obviously, the character of the distribution of ion-exchange palladium over the cross section of a fiber exerts an effect on the rate and degree of its extraction with a solution of thiocarbamide. It is believed that the $PdCl_4^{2-}$ anions located nearby the outer fiber surface will easily form a complex compound with thiocarbamide and be extracted from the ion exchanger without steric hindrances.

Figure 1 shows the dependence of the degree of palladium extraction on the volume of passed eluent for catalysts based on the chloride forms of fibrous anion exchangers. It can be seen that ion-exchange palladium was extracted from the chloride form of FIBAN A-6 more rapidly and completely than from the same form of FIBAN A-5. Obviously, the observed effect is a consequence of differences in the nature of functional groups in the supports. The major portion of functional groups in the FIBAN A-6 anion exchanger consists of quaternary alkylammonium groups of the following structure:



It is likely that the high rate of exchange at quaternary groups facilitates the localization of $PdCl_4^{2-}$ ions in the peripheral region of the fiber cross section; because of this, the extraction of these ions with a solution of thiocarbamide is facilitated. Another reason for the easy extraction of ion-exchange palladium from FIBAN A-6 can be the fact that the bulky quaternary amino groups hamper the migration of the $PdCl_4^{2-}$ anions deep into the fiber.

Figure 2a shows the results of the determination of the degree of Pd^{2+} extraction from unreduced catalyst samples containing 0.15% Pd on the FIBAN A-5 fibrous anion exchanger in the oxalate, butyrate, succinate, tartrate, and citrate forms. As can be seen, the degree of the extraction of ion-exchange palladium from all of the samples based on the carboxylate forms of anion exchangers was noticeably higher than that from a control sample based on the chloride form. The maximum degree of extraction (95%) was reached in a sample based on the citrate form of FIBAN A-5.

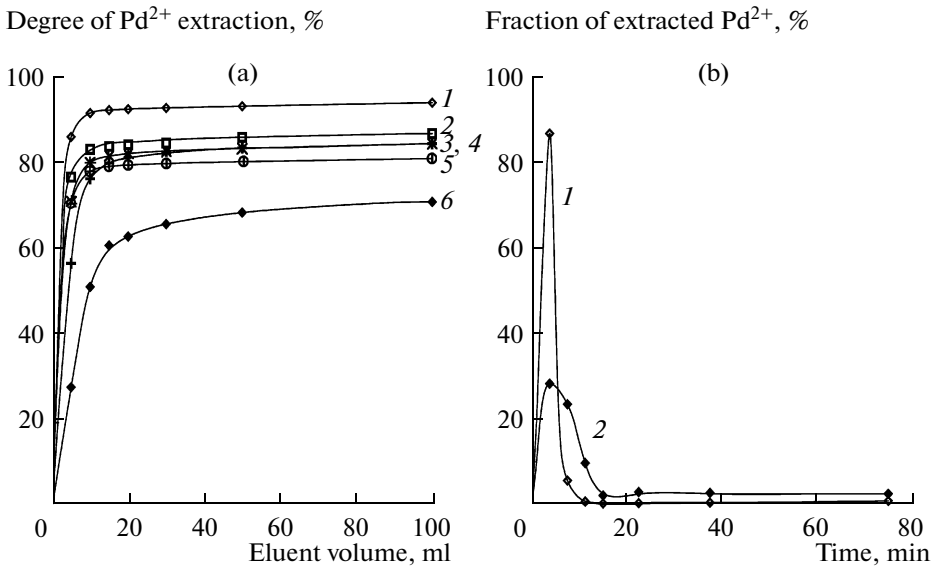


Fig. 2. (a) Degree of Pd^{2+} extraction from unreduced 0.15% Pd/FIBAN A-5 catalyst samples as a function of the volume of passed eluent: (*1*) citrate, (*2*) tartrate, (*3*) butyrate, (*4*) succinate, (*5*) chloride, and (*6*) oxalate forms of the anion exchanger. (b) Effect of the elution time on the fraction of Pd^{2+} extracted from unreduced 0.15% Pd/FIBAN A-5 catalyst samples: (*1*) citrate and (*2*) chloride forms of the anion exchanger.

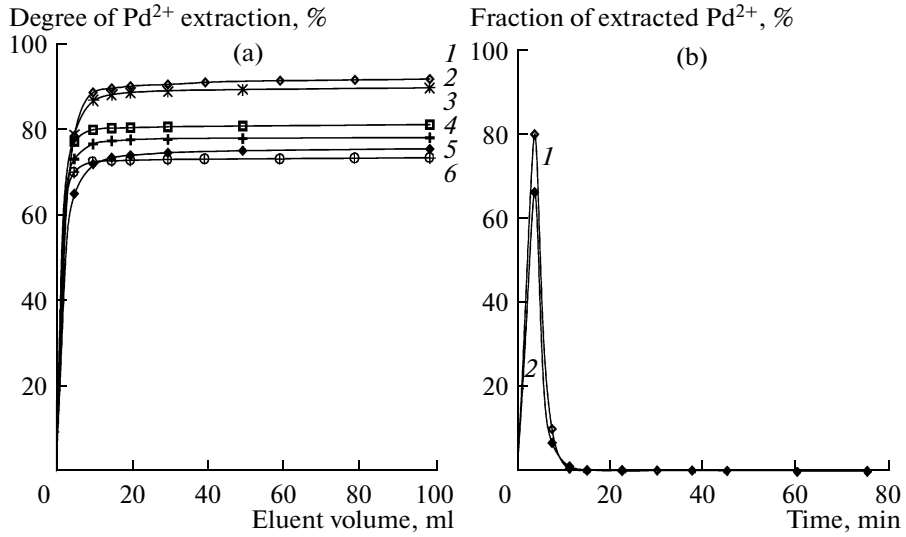


Fig. 3. (a) Degree of Pd^{2+} extraction from unreduced 0.15% Pd/FIBAN A-6 catalyst samples as a function of the volume of passed eluent: (*1*) citrate, (*2*) succinate, (*3*) tartrate, (*4*) butyrate, (*5*) chloride, and (*6*) oxalate forms of the anion exchanger. (b) Effect of the elution time on the fraction of Pd^{2+} extracted from unreduced 0.15% Pd/FIBAN A-6 catalyst samples: (*1*) citrate and (*2*) chloride forms of the anion exchanger.

The kinetic curves of the extractions of ion-exchange palladium from samples based on the FIBAN A-5 anion exchanger in the citrate and chloride forms (Fig. 2b) are strongly different in shape. Palladium was extracted almost completely from a catalyst based on the citrate form of the support in 10–11 min (curve *1*, a sharp peak), whereas it was extracted much more slowly from a sample based on the chloride form (curve *2*, a diffuse peak). The major portion of palladium (85–86%) was extracted in the first 15 min, and the remaining part was extracted at a low rate in the course of the entire experiment. It is obvious that the diffuse peak of the sample based on the chloride form suggests that the $PdCl_4^{2-}$ anions in this sample occurred both on the surface and in the bulk of the ion-exchanger fiber.

Table 2. Results of the X-ray microanalysis of the fiber surface for palladium

Sample	Test region	Spectrum	Concentration of Pd, wt % on a dry sample basis
1.0% Pd/FIBAN A-6, chloride form	1	1	0.98
		2	1.31
		3	0.85
	Average value		1.05
	2	1	0.49
		2	1.06
		3	1.08
	Average value		0.88
1.0% Pd/FIBAN A-6, citrate form	1	1	1.22
		2	0.87
		3	1.45
	Average value		1.18
	2	1	1.66
		2	1.13
		3	1.38
	Average value		1.39

Figure 3a shows the results of the determination of the degree of Pd^{2+} extraction from the unreduced catalyst samples based on the FIBAN A-6 anion exchanger in various carboxylate forms. The degree of the extraction of ion-exchange palladium increased, as compared with the control sample (with the exception of the oxalate form); however, this effect is not as pronounced as that in the case of FIBAN A-5. This is natural because ion-exchange palladium was extracted much more intensely from a sample based on the chloride form of FIBAN A-6 (control sample) than from an analogous sample based on FIBAN A-5 (Fig. 1).

The maximum degree of the extraction of ion-exchange palladium in this series was also reached in the catalyst sample based on the citrate form of the anion exchanger (94.2%).

The kinetic curves of the extraction of Pd^{2+} from the samples based on the FIBAN A-6 anion exchanger in the citrate and chloride forms have similar characters (Fig. 3b). The major portion of palladium was rapidly extracted from the samples (approximately in 10 min); however, in the case of the sample based on the citrate form, the fraction of initially extracted palladium was noticeably higher; this fact suggests the greater accessibility of palladium to extraction with thiocarbamide.

Because the dimensions of the complex of thiocarbamide with the $PdCl_4^{2-}$ anion are relatively great, its diffusion from the bulk of the ion exchanger to the surface is difficult because of steric hindrances. Therefore, the high values of rate and degree of extraction of ion-exchange palladium from the ion exchanger are characteristics that suggest the preferred localization of the $PdCl_4^{2-}$ anions in a thin subsurface layer of the fiber.

Data shown in Figs. 2 and 3 indicate that citric acid is the best modifier of FIBAN A-5 and FIBAN A-6 anion exchangers, which ensures the localization of $PdCl_4^{2-}$ anions in a thin subsurface layer of the fiber. Obviously, this is due to the circumstance that the citrate ion is bulkier than the other carboxylate ions used in this study. It is believed that the citrate ions predominantly sorbed in a subsurface layer of the fiber create steric hindrances for the sorption of other ions from solution, in particular, preventing the penetration of the $PdCl_4^{2-}$ ions deep into the fiber.

It was interesting to obtain data on the distribution of palladium in the bulk and on the surface of the FIBAN A-6 anion-exchanger fiber in the chloride and citrate forms by X-ray microanalysis. The following two unreduced catalyst samples were specially prepared for this purpose: 1.0% Pd/FIBAN A-6 (chloride form) and 1.0% Pd/FIBAN A-6 (citrate form).

It was found that the intensity of palladium emission over the cross section of the fiber in the test samples was at a background level. This can be in the case of supported palladium predominantly localized in a thin subsurface film of the fiber (to 0.1 μm in thickness), which cannot be detected by the instrument.

Upon scanning the surface of the samples (three sections were selected for analysis according to a random law), we found that the average concentration of palladium in a thin subsurface layer of the fiber of the 1.0% Pd/FIBAN A-6 (chloride form) catalyst was noticeably smaller than that in an analogous sample based on the citrate form of the anion exchanger: 1.0 and 1.3 wt %, respectively (Table 2). The experimental data indicate that palladium in the catalyst sample based on the citrate form of the anion exchanger was localized nearer to the outer fiber surface than in the sample based on the chloride form. Setting the palladium content of the subsurface layer of the fiber in the 1.0% Pd/FIBAN A-6 (citrate form) catalyst at 100%, the palladium content of this layer in the sample based on the chloride form was about 77%. These values correlate with the results obtained upon the extraction of

Table 3. Activity of palladium-containing catalysts based on the chloride and citrate forms of FIBAN A-5 and FIBAN A-6 in the process of water deoxygenation*

Catalyst	Concentration of H_2 in water, μg/l		Concentration of O_2 in water, μg/l	
	before the reactor	after the reactor	initial water	purified water
0.15% Pd/FIBAN A-5 (chloride form)	680	65	4600	18
0.15% Pd/FIBAN A-5 (citrate form)	650	35	4300	2
0.15% Pd/FIBAN A-6 (chloride form)	720	80	4300	11
0.15% Pd/FIBAN A-6 (citrate form)	550	15	4300	1

* Experimental conditions: reaction zone volume, 200 cm^3; pressure, 0.3 MPa; and purified water flow rate, 45 l/h; water temperature, 15°C.

ion-exchange palladium from the samples with a solution of thiocarbamide (Fig. 3).

Table 3 summarizes the results of the determination of the activity of reduced catalyst samples based on the chloride and citrate forms of FIBAN A-5 and FIBAN A-6 in the process of water deoxygenation (the activity was evaluated from the residual oxygen content of purified water). All of the samples listed in Table 3 provided a sufficient degree of water deoxygenation, less than 20 μg/l of residual oxygen. However, catalysts based on the citrate form of the anion exchanger were superior to the samples prepared based on the chloride form in terms of activity. In the presence of the samples based on the citrate form, the residual oxygen content was as low as 1–2 μg/l, which is lower than the corresponding characteristic of a well-known granulated catalyst by at least an order of magnitude [1, 2].

Note that the catalysts based on the citrate form more rapidly reached steady-state operating conditions. This can be clearly seen in the plots shown in Fig. 4. The catalyst based on the citrate form of the FIBAN A-6 anion exchanger (curve *2*) decreased the concentration of residual oxygen in purified water to 20 μg/l even at the 60th minute after the onset of operation. A much longer time should be spent to reach the above degree of water deoxygenation in the case of the catalyst based on the chloride form of the anion exchanger (curve *1*).

Thus, the procedure developed of the preparation of the fibrous palladium-containing catalyst resulted in the predominant localization of $PdCl_4^{2-}$ anions and, correspondingly, Pd^0 clusters in a thin subsurface layer of the fiber. The best results of the localization of palladium in the thin subsurface layer of a fibrous support were obtained with the use of citric acid as a modifier. The activity of the samples of fibrous palladium-con-

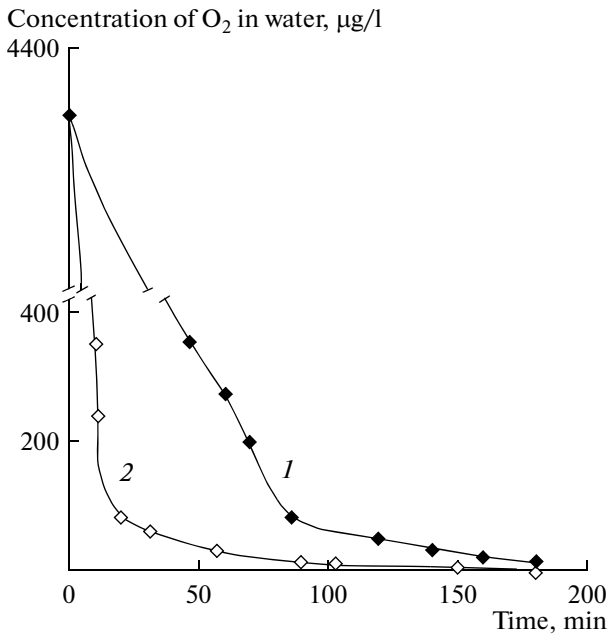


Fig. 4. Dependence of the residual oxygen content of purified water on catalyst operation time: (*1*) 0.15% Pd/FIBAN A-6 (chloride form) and (*2*) 0.15% Pd/FIBAN A-6 (citrate form). Water flow rate, 45 l/h; oxygen concentration in the water being purified, 4.3 mg/l; and water temperature, 15°C.

taining catalysts based on the citrate forms of anion exchangers was noticeably higher than the activity of the samples based on the chloride forms.

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