Kinetics and Catalysis, Vol. 43, No. 6, 2002, pp. 862–867. Translated from Kinetika i Kataliz, Vol. 43, No. 6, 2002, pp. 928–933.
Original Russian Text Copyright © 2002 by Yegiazarov, Radkevich.

Effect of the Cationic Form of a Fiban K-1 Fibrous Sulfo Cation Exchanger on the Degree of Reduction and Activity of Palladium in the Oxidation of Hydrogen

Yu. G. Yegiazarov and V. Z. Radkevich

Institute of Physicoorganic Chemistry, Belarussian Academy of Sciences, Minsk, 220072 Belarus

Received December 26, 2001

Abstract—The effect of the nature of the exchanged cation M^{z+} ($M^{z+} = Li^+$, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}) of a Fiban K-1 fibrous sulfo cation exchanger on the degree of reduction of the immobilized complex cations $[Pd(NH_3)_4]^{2+}$ to Pd^0 was studied. A linear correlation was found between the degree of palladium reduction and the difference of the relative electronegativities of atoms that participate in the $O–M^{z+}$ bond. The activity of the catalysts in the oxidation of H_2 depends on the degree of palladium reduction.

INTRODUCTION

Granular sulfo cation exchangers are in wide industrial use as the catalysts of acid–base reactions. In recent years, they have attracted the attention of researchers as supports for metal-containing catalysts used in redox reactions [1–3].

In many cases, the rate of reaction in catalytic systems based on granular ion exchangers depends on internal diffusion. Thus, it is reasonable to reduce the diameter of granules. However, this results in an increase in the hydraulic resistance of a catalyst bed.

The use of fibrous ion exchangers, in which the fiber diameter is much smaller than the size of a granule (by approximately one order of magnitude), in catalytic processes considerably decreases diffusion limitations and, correspondingly, increases the rate of mass-exchange processes.

Previously [4–6], we found that a palladium catalyst prepared based on a Fiban K-1 fibrous sulfo cation exchanger in the barium form exhibited a high activity in the oxidation of hydrogen.

Currently available publications are almost not concerned with important problems of the effects of the physicochemical properties of sulfo cation exchangers, in particular, of their cationic forms, on the activity of supported metal catalysts.

It is well known that solid supports (metal oxides and zeolites) can significantly affect the electronic state, chemisorption properties, and, consequently, catalytic activity of a supported metal [7–9].

The effect of a support on the state of a metal appears even at the stage of catalyst preparation; it manifests itself in different degrees of metal reduction on supports that differ in nature. Thus, in the case of supporting palladium on silica gel from a $[Pd(NH_3)_4]Cl_2$ solution, complete reduction did not take place even at 100°C [10]. According to Gubitosa *et al.* [10], this fact can be explained by the formation of a strong bond between the above complex and the support.

The aggregation mechanism of reduced palladium also depends on the metal–support interaction: the migration of atoms corresponds to strong interaction, whereas the migration of particles corresponds to weak interaction [11].

In this context, it is of interest to study how the above regularities manifest themselves in the synthesis and activation of metal-containing catalysts based on organic ion-exchange resins such as sulfo cation exchangers.

Because inorganic oxide supports of different nature exhibit different degrees of interaction with a supported metal, it is reasonable to study metal-containing ion exchange catalysts that differ in the properties of supports. These properties can be conveniently varied by changing the cationic form of the support. In this case, the same parent ion exchanger may be used for preparing samples with different properties, and possible effects of foreign factors on the catalytic system are thereby eliminated.

In this study, we synthesized palladium catalysts based on various cationic forms of a fibrous sulfo cation exchanger and studied the effect of the nature of an exchanged cation on the degree of metal reduction, on metal distribution over the fiber cross section, and on the activity in hydrogen oxidation.

EXPERIMENTAL

The Fiban K-1 fibrous sulfo cation exchanger (H form) was prepared by the bulk radiation grafting of a copolymer of styrene (98%) and divinylbenzene (2%) to a polypropylene staple followed by the sul-

Characteristics of the synthesized catalysts

Sample no.	Catalyst	Palladium content, wt %	S*, %	A**, cm^3 (g Pd)$^{-1}$ s^{-1}
First series of catalysts				
1	Pd/Li–K-1	0.245	44	15.8
2	Pd/Na–K-1	0.230	55	17.0
3	Pd/Rb–K-1	0.197	58	18.7
4	Pd/Cs–K-1	0.176	64	21.3
5	Pd/Mg–K-1	0.240	38	15.2
6	Pd/Ca–K-1	0.235	49	16.8
7	Pd/Ba–K-1	0.205	48	16.2
Second series of catalysts				
8	Pd/Ba–K-1	0.250	10	4.8
9	″	″	21	6.1
10	″	″	30	11.5
11	″	″	39	15.4
12	″	″	50	16.6

Note: Activation conditions, T_{He} = 130°C, 1 h; T_{H_2} = 130°C, 1.5 h.

* The degree of palladium reduction.

** The reactor output per gram of Pd.

fonation of the resulting matrix with concentrated sulfuric acid [12].

Based on the hydrogen form of K-1 with an exchange capacity of 3.0 mg-equiv/g, the completely replaced M^{z+} forms ($M^{z+} = Li^+$, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}) were prepared by passing 1 N metal chloride solutions through a column with the ion exchanger until pH in the filtrate became equal to pH in the initial solution. After the exchange, the samples were washed with distilled water until Cl^- ions were absent from the wash water and dried at 40°C (4 h). Two series of catalysts were prepared.

First series of catalysts. The exchange of Li^+, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} cations for $[Pd(NH_3)_4]^{2+}$ cations was performed by the treatment of a sample of the ion exchanger in a corresponding form with a calculated volume of a tetraamminepalladium(II) chloride solution with a low concentration (0.001 N). This procedure provided uniform palladium distribution over the fiber cross section. The sample weights of the initial ion exchangers were varied taking into account the gram-equivalent weights of different cationic forms of the ion exchanger so that the concentration of tetraamminepalladium(II) cations in the ion-exchanger phase after the exchange was 1.5% of the exchange capacity in all of the samples. In this case, catalysts with equal ratios between the equivalent fractions of ions $X_{M^{z+}}/Y_{[Pd(NH_3)_4]^{2+}}$ in the ion-exchanger phase but with different palladium contents (see table) were obtained because the exchanged cations (M^{z+}) are different in weight.

An ion-exchanger sample was preexposed to distilled water until complete swelling. Next, it was squeezed on filter paper and the exchange was performed with intense stirring at room temperature for 30 min. The pH value of the contacting solution was maintained at a level of 8–8.5 (it is well known [13] that the complex cation $[Pd(NH_3)_4]^{2+}$ is stable in an aqueous ammonia solution at pH ≥ 8).

After the exchange, the samples were dried at 40°C (4 h); next, they were heated in a helium flow (130°C; 1 h) and reduced with hydrogen at the specified temperature for 1.5 h.

The concentration of palladium in solutions before and after the exchange was monitored using a published spectrophotometric procedure [14].

The degree of reduction S (the percentage of reduced palladium in the samples) was determined by the treatment of the samples with an excess of a 1 N NaCl solution until the ion-exchange form of palladium

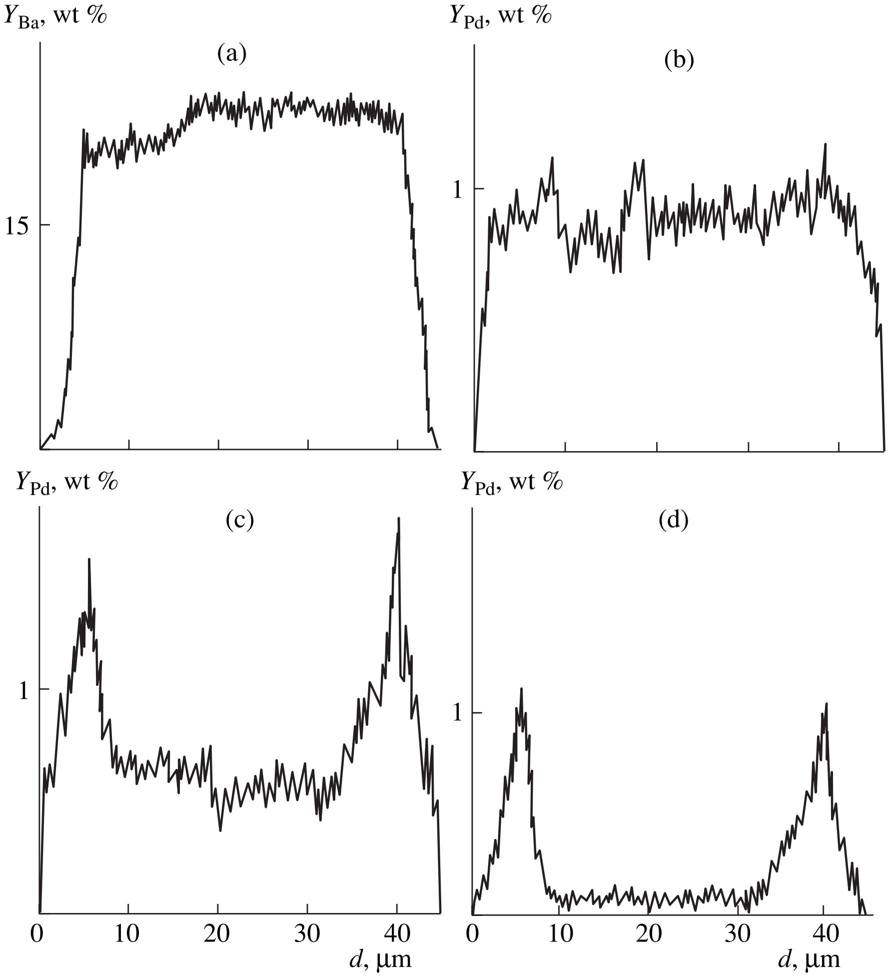


Fig. 1. (a) Barium and (b–d) palladium distribution over the fiber cross section in the samples of (a) the Ba form of the ion exchanger and a 1.0 Pd/Ba-K-1 catalyst (b) before or (c) after activation and (d) after the removal of ion-exchanged palladium (Y_{Ba} is the barium content; Y_{Pd} is the palladium content; and d is the fiber diameter).

was completely transferred to the solution with the subsequent determination of palladium concentration.

Second series of catalysts. A base catalyst containing 0.25 wt % Pd was synthesized based on the Ba form of the Fiban K-1 sulfo cation exchanger (under the same preparation conditions as in the first series of catalysts). Individual weighed portions of this catalyst were heated in a helium flow at 130°C for 1 h and then reduced in a hydrogen flow at the specified temperature. However, as distinct from the first series of catalysts, the duration of reduction was varied within a range of 0.25–1.5 h. Thus, 0.25% Pd/Ba-K-1 catalyst samples with different degrees of palladium reduction were prepared (see table).

The distribution of palladium over the fiber cross section was determined by X-ray microanalysis on a Cameca MS-46F instrument. In accordance with the resolving power of the instrument, samples containing 1.0 wt % Pd were prepared.

The X-ray diffraction analysis of the test samples was performed on a DRON-1 instrument using copper radiation.

The experiments on hydrogen oxidation in the presence of the synthesized catalysts were performed in a glass flow reactor (20 mm i.d.) with automatically controlled electric heating. The design of the reactor allowed us to measure the temperature throughout the height of a catalyst bed [5]; this is of particular importance in the studies of exothermic reactions.

In the experiments with catalysts from the first series, which were different in palladium contents per unit weight of the ion exchanger, samples with different weights (from 0.9 to 1.2 g) were placed in the reactor in order to obtain equal palladium weights in all of the loadings.

In the studies of catalysts from the second series, which contained equal amounts of palladium, 1-g samples were loaded into the reactor.

In all cases, the height of the catalyst bed was kept on one level (~40 mm) by different degrees of compaction of the ion exchanger.

The relatively high ratio (1 : 2) between the diameter and the height of the catalyst bed and the low concentration of hydrogen in the gas flow supplied to the reactor allowed us to exclude a detectable temperature gradient along the height of the catalyst bed.

The test samples were heated in a flow of dried helium at 130°C for 1 h; next, the temperature was decreased to 100°C; the helium flow was stopped, and a gas mixture (3 vol % H_2 in air) was supplied to the reactor at a flow rate of 100 cm^3/min. After 15–20 min, the gas was sampled and analyzed on a Gazokhrom-31 chromatograph. The conversion of hydrogen was calculated by the difference between its concentrations in gas samples of equal volumes before and after the reactor.

The activity of the catalysts was characterized by the reactor output per unit weight (1 g) of palladium and calculated by the equation

$$A = V_{H_2}\alpha/m_{Pd}\ (\mathrm{cm^3\ (gPd)^{-1}\ s^{-1}}),$$

where V_{H_2} is the flow rate of hydrogen (cm^3/s) and α is the conversion of hydrogen (volume fraction).

RESULTS AND DISCUSSION

Under identical experimental conditions, the catalyst activity may be affected by the degree of reduction and the dispersity of palladium, the distribution of particles over the fiber cross section, and the mass transfer of reactant molecules to active centers.

Data on the distribution of Ba^{2+} cations over the fiber cross section, which is shown in Fig. 1a, indicate that functional groups are uniformly distributed in the bulk of the ion exchanger. Analogous distribution was also observed for $[Pd(NH_3)_4]^{2+}$ cations after ion exchange (Fig. 1b). The reduced sample is characterized by an increased concentration of palladium in the fiber surface layer (Fig. 1c). Consequently, the migration of reduced metal particles occurs in the activation of the catalyst with the predominant distribution of the metal at the periphery of the fiber cross section.

A comparison of data given in Figs. 1c and 1d demonstrates that, on the activation of the catalyst under the above conditions, a considerable portion of palladium was not reduced, and it remained at the ion-exchange positions of the ion exchanger. The major portion of the reduced metal was concentrated at the peripheral area of the fiber cross section 10–15 μm in thickness.

The reflections of palladium metal were absent from the X-ray diffraction patterns of reduced catalysts; this fact is indicative of the high dispersity of its particles ($d_{Pd} < 50$ Å).

The palladium contents of catalysts from the first series, which were prepared based on various cationic forms of the ion exchanger (see the table), were 0.176–0.245 wt % (in accordance with the synthesis conditions, the palladium contents in the equivalent of the ion exchanger were equal in all of the samples). The values of *S* in the catalysts were significantly different and varied from 38 to 64%.

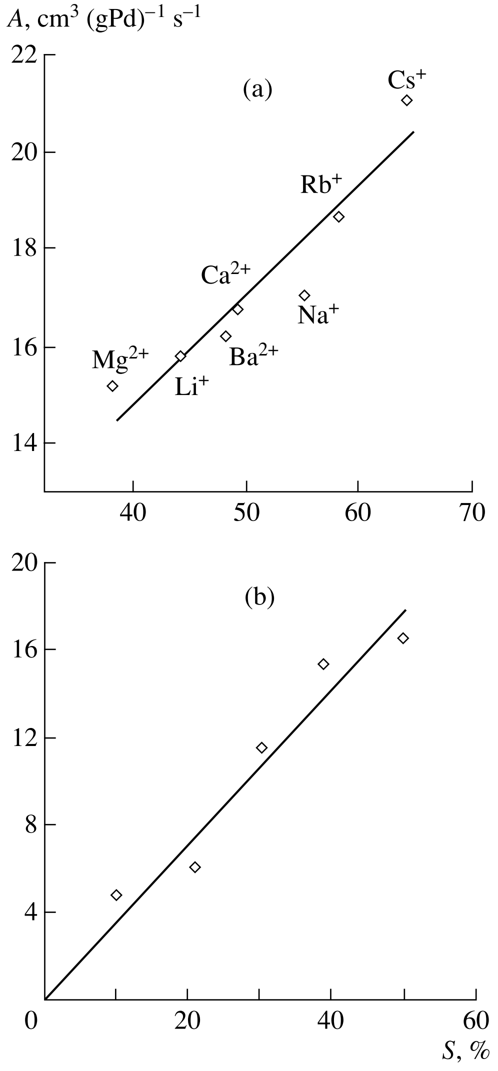


Fig. 2. Reactor output (per gram of Pd) *A* as a function of the degree of palladium reduction *S* in catalysts from the (a) first and (b) second series.

Figure 2a demonstrates that catalysts from the first series exhibited a linear relationship between the degree of palladium reduction and the activity in hydrogen oxidation.

Differences in the catalytic activity of the test samples can be due not only to different degrees of palladium reduction but also to different rates of the mass transfer of reactant molecules to active centers. To find which of the two factors has a determining effect on the apparent activity, we performed experiments on the oxidation of hydrogen on catalysts from the second series.

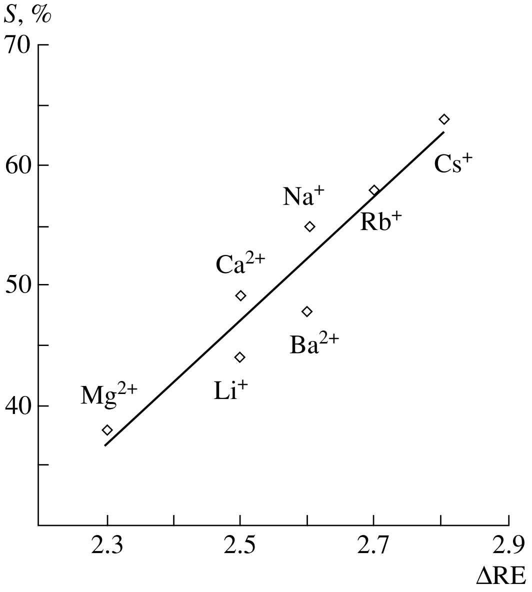


Fig. 3. Degree of palladium reduction *S* as a function of the difference between the relative electronegativities (ΔRE) of atoms that participate in O–M^{z+} bond formation.

Because samples of this series were prepared based on the same ion exchanger (Ba form) and they contained equal amounts of palladium (0.25% of the support weight) and differed in only degrees of metal reduction, we believe that they exhibit identical diffusion properties.

Data shown in Fig. 2b indicate that, as in the case of catalysts from the first series, the degree of palladium reduction is a linear function of the activity in hydrogen oxidation. Moreover, catalysts based on different cationic forms of the ion exchanger with similar values of *S*, for example, sample nos. 5 and 11 or 6 and 12 (see table), are characterized by almost equal values of the reactor output per gram of palladium.

The above data suggest that the degree of palladium reduction rather than the mass transfer of reactants to active centers is the predominant factor in the apparent activity of the catalysts.

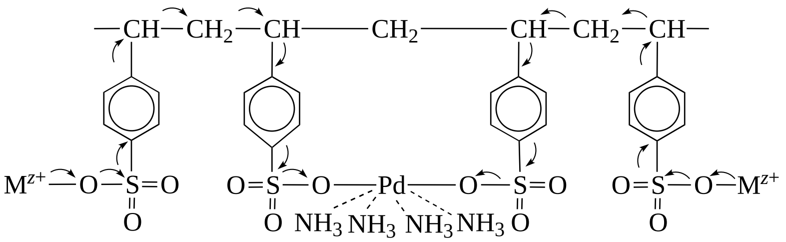
In accordance with the values of *S*, the cationic forms of the ion exchanger are arranged in the following order:

Cs–K-1 > Rb–K-1 > Na–K-1 > Ca–K-2
≈ Ba–K-1 > Li–K-1 > Mg–K-1.

It is of interest how the nature of the exchanged cation affects the reduction of tetraamminepalladium(II) complexes immobilized on the ion exchanger to Pd^0.

It is well known that, the greater the difference between the electronegativities of participating atoms, the higher the polarization and bond ionicity [15]. Consequently, the effective negative charge at oxygen atoms bound to palladium is lower than that at oxygen atoms bound to alkali and alkaline-earth metal cations.

Taking into account a number of circumstances (the deep dehydration of the ion exchanger in the course of catalyst activation, which affects the effective charge of exchangeable cations; the collective interactions of functional groups charged with cations of different nature with the ion-exchanger matrix; and the occurrence of substituents that are the salt forms of benzenesulfonic acid at the macromolecular chain), it is believed that the states of the fragments of the system can be equalized by electron density redistribution. That is, it is believed that electron density in the macromolecule of the sulfo cation exchanger can be shifted to relatively long distances in accordance with the following scheme:



As a result, the O–Pd bond ionicity and strength decrease to facilitate the reduction of the metal.

The correctness of this approach to an explanation of experimental data was supported by the dependence of the degree of palladium reduction on the difference between the relative electronegativities (ΔRE) of atoms that participate in O–M^{z+} bond formation (Fig. 3).

Thus, the results of this study suggest an analogy between supported metal catalysts prepared on the basis of solid oxide supports and organic ion exchangers: the degree of reduction of a metal and its catalytic activity depend on the physicochemical properties of the support, which are responsible for the metal–support interaction.

REFERENCES

1. Jerabek, K.J., *Mol. Catal.*, 1989, vol. 55, p. 247.
2. Bar-Sela, G. and Warshawsky, A., *J. Polym. Sci., Part A: Polym. Chem.*, 1990, vol. 28, p. 1303.
3. Biftis, A., Corain, B., Cvengrosova, Z., *et al.*, *Appl. Catal.*, 1995, vol. 124, p. 335.

4. Yegiazarov, Yu.G., Soldatov, V.S., Radkevich, V.Z., *et al.*, *Tez. dokl. XVI Mendeleevskogo s"ezda po obshchei i prikladnoi khimii* (Proc. XVI Mendeleev Congress on General and Applied Chemistry), St. Petersburg, May 25–29, 1998, vol. 2, p. 292.
5. Yegiazarov, Yu.G., Radkevich, V.Z., Johann, J., *et al.*, *React. Funct. Polym.*, 2000, vol. 44, p. 145.
6. Radkevich, V.Z., Shunkevich, A.A., Kistanova, I.E., *et al.*, *Zh. Prikl. Khim.*, 2000, vol. 73, no. 11, p. 1861.
7. Zakumbaeva, G.D., Zakarina, N.A., Beketaeva, L.A., and Naidin, V.A., *Metallicheskie katalizatory* (Metal Catalysts), Alma-Ata, 1982.
8. Anderson, Dzh., *Struktura metallicheskikh katalizatorov* (Structure of Metallic Catalysts), Moscow, 1978.
9. Slinkin, A.A., *Itogi Nauki Tekh., Kinet. Katal.*, 1982, vol. 10, p. 5.
10. Gubitosa, G., Berton, A., Camia, M., and Pernicone, N., *Proc. 3rd Int. Symp. Lauvainla-Nauve*, Elsevier, 1983, p. 431.
11. Baker, R.T.K., Prestridge, E.B., and Gasten, R.L., *J. Catal.*, 1979, vol. 56, no. 3, p. 390.
12. Soldatov, V.S., Pokrovskaya, A., and Martsinkevich, R.V., *Zh. Prikl. Khim.*, 1984, vol. 5, no. 9, p. 2030.
13. Zamanova, L.P., Aleksandrova, I.L., and Khadzhiev, S.N., *Tez. dokl. II Vsesoyuz. konf. "Primenenie tseolitov v katalize"*(Proc. II All-Union Conf. on Applications of Zeolites in Catalysis), Moscow, 1981, p. 277.
14. Veshtort, V.Z., Shingel', I.A., Savchits, M.F., and Yegiazarov, Yu.G., *Zavod. Lab.*, 1989, no. 10, p. 6.
15. Haberditzl, W., *Bausteine der Materie und chemische Bindung*, Berlin: VEB Deutscher Verlag der Wissenschaften, 1972.