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Study of Palladium Complexes with Chitosan and Its Derivatives as Potential Catalysts for Terminal Olefin Oxidation

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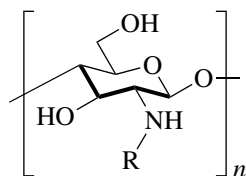
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Abstract—FTIR spectroscopy and XPS are used to study palladium complexes with various forms of chitosan: initial and modified by glutaric aldehyde. IR bands are identified that are related to the Pd–N and Pd–O bonds. A difference between the spectra of complexes obtained by the methods of adsorption and coprecipitation of chitosanium hydrochloride with the tetrachloropalladate ion is found. It is shown that the systems studied can be used as catalysts for terminal olefin oxidation by oxygen in the presence of H_2O_2. In the course of the reaction, the complexes undergo redox transformations without breaking the structure of the complex or metal transfer to the reaction mixture. The use of heterogenized Pd(II) complexes as catalysts in terminal olefin oxidation leads to the formation of oxidation and isomerization products, similarly to the case of homogeneous oxidation.

INTRODUCTION

The use of transition metal complexes immobilized on various support materials in catalysis combines the advantages of homogeneous and heterogeneous catalytic systems and makes it possible to carry out processes under mild conditions with a high selectivity [1]. The broadening of the spectrum of support materials and processes as well as the involvement of new substrates in the reactions of heterogenized metal complexes is an important current problem. Biopolymers such as cellulose, chitin, and chitosan, find recent use as support materials for the heterogenization of homogeneous catalysts [2, 3].

Chitosan (deacetylated chitin) is a linear polysaccharide with a polymer chain consisting of β-1,4-linked glucosamine residues.

It has several unique properties that make it advantageous for use over other polymer support materials [4–6]:

(1) Chitosan is nontoxic, readily decomposes in natural biological environments, and is compatible with living organism (both plant and animal) cells;

(2) The polymeric matrix is capable of providing the high dispersity of a metal;

(3) Chitosan has various functional groups;

(4) Chitosan is resistant to such oxidants as air, oxygen, and dilute hydrogen peroxide;

(5) The mechanical strength of chitosan is rather high; and

(6) Valuable catalyst components can easily be separated from the spent catalyst by burning out the organic support and the further extraction of metals.

The thermal stability of chitosan is not high (it decomposes at 250°C), but one of the requirements to modern catalysts is their capability of operating under mild conditions.

Although chitosan is broadly used in various industries, data on its applications in catalysis are currently scarce. Chitosan and chitin complexes with platinum group metals are used in the reactions of heterogeneous catalytic hydrogenation (including asymmetric hydrogenation) [7, 8]. Rare earth metal complexes of chitosan are used in polymerization reactions (with ethylene oxide, propylene oxide, methyl metacrylate, and epichlorohydrin as monomers) [9]. The immobilization of various enzymes (proteases, oxidases, etc.) on chitosan and chitin matrices makes it possible to considerably improve their stability and efficiency [10]. Data on heterogeneous catalytic oxidation by metal complexes immobilized on chitosan are practically absent in the literature.

Synthesis of carbonyl compounds by the oxidation of terminal olefins by oxygen in the presence of Pd(II) is well known in homogeneous catalysis. The physicochemical foundations of this process were developed by Moiseev and co-workers in the early 1970s [11]. Analysis of literature data shows that current research along these lines focuses both on the search for new systems for reoxidation and on heterogenization of the process. Thus, in the mid-1990s a new series of papers devoted to the use of conducting polymers (polyaniline and polypyrrol) as supporting materials for Pd(II)

Chemical composition of chitosans (wt %)

Element	Initial chitosan	Modifies chitosan	Calculated*	Ref. data* [15]
C	41.35	44.73	53.87	54.03
H	6.35	6.37	7.81	7.68
N	7.26	5.30	5.71	5.80

* For chitosan with a degree of deacetylation of 100%.

immobilization were published. Heterogeneous systems thus obtained were used in the oxidation of terminal olefins C_9 and with longer carbon chains [1, 12].

The main goal of this work was to obtain heterogenized palladium complexes on various forms of chitosan, elucidate their structures, and evaluate the possibility of their use in the oxidation of terminal olefins (hexene-1 and heptene-1). To reach this goal, we studied changes in the coordination and charge states of palladium in the course of model stages of this reaction.

Chitosan and its derivatives are rather complex objects for a structural study. Therefore, the inclusion of that or other group in a chitosan molecule has been most frequently proven by elemental analysis. ^{13}C NMR spectroscopy was used for the first time in the study of chitosan in the 1990s, whereas ^{1}H NMR spectroscopy has not been used because of the complexity of the resulting spectra [6]. Chitosan metal complexes cannot be studied by methods such as X-ray phase and structural analyses, which are usually used in the studies of organometallic and coordination compounds, because such complexes are X-ray amorphous. Therefore, we chose elemental analysis, FTIR spectroscopy, and XPS for our study.

EXPERIMENTAL

Chitosan complexes of Pd(II) were prepared, since they have the simplest structure. However, it is known that the oxidation of terminal olefins needs an initial acidic background $[H^+] = 0.1$ M, which initiates the reaction. Nonmodified chitosan and its complexes are readily soluble in dilute acids. Therefore, the resulting polymer modification should be stable in the interval $[H^+]$ 0.05–0.1 M. To obtain insoluble forms of chitosan, glutaric aldehyde as a cross-linking agent is used [13]. Chitosan was thus modified by glutaric aldehyde, and palladium complexes with this modified chitosan were obtained.

Preparation and Modification of Support Materials

Nonmodified chitosan. To prepare the catalysts, we used chitosan (made in Korea; molecular weight,

100000–150000; degree of deacetylation of amino groups, 70%; moisture content, 3 wt %), prepared from crab shells without additional purification. The main characteristics of the initial and modified chitosan are presented in the table.

Modified chitosan. To prepare chitosan modified by glutaric aldehyde, we used methods described earlier [13–15]. The initial chitosan was dissolved in 0.1 M HCl to obtain a 1.5 wt % solution. The resulting solution (60 ml) was added to 60 ml of hexane containing 5 wt % SPAN® 60 (sorbitane monostearate, Fluka AG) emulsifier. The mixture was stirred at 60°C at a rate of 3000 rpm until the formation of an emulsion. Then, the stirring rate was decreased to 500 rpm and 13 ml of a 25% aqueous solution of glutaric aldehyde was added in drops for 1 h (the binding degree GA/–NH_2 was 0.64 mol/mol). The stirring rate was kept constant (500 rpm) for 4 h until complete binding. To remove SPAN® 60, the resulting polymer was filtered and washed several times in distilled water at 80°C and hexane at 55°C. Then, the polymer was dried in air for 48 h.

Preparation of Heterogenized Palladium Complexes with Chitosan and Its Derivatives

Heterogenized palladium complexes were prepared by coprecipitation and adsorption methods [16, 17].

Adsorption method. Polymer particles were placed in an aqueous solution of Na_2PdCl_4 (with 2 wt % with respect to the polymer). The solution was stirred for 1 h, and then the particles were filtered, washed with distilled water several times, and dried in air for 24 h.

Coprecipitation method. A homogeneous solution of a palladium complex with chitosan. The necessary amount of palladium chloride (containing 2 wt % Pd with respect to a polymer) was dissolved in 60 ml of 0.1 M HCl. One gram of nonmodified chitosan was added to the resulting solution, which was then stirred until the formation of a homogeneous gel-like mixture.

The resulting homogeneous solution of the palladium chitosan complex was added in drops to a 0.5 M solution of NaOH. The resulting particles were allowed to stay in an alkali for 2 h, filtered, washed several times with distilled water until pH 7, and dried in air for 48 h.

Preparation of the template palladium complex with chitosan, modified by glutaric aldehyde. A homogeneous palladium complex with chitosan (60 ml), prepared as described above, was mixed with the same amount of hexane containing 5 wt % SPAN® 60. The mixture was stirred at 60°C at a rate of 3000 rpm until emulsion formation. Then, the stirring rate was decreased to 500 rpm and 13 ml of a 25% aqueous solution of glutaric aldehyde was added in drops for 1 h (the binding degree GA/–NH_2 was 0.64 mol/mol). The stirring rate was kept constant (500 rpm) for 4 h until the binding procedure was done. To remove SPAN® 60, the resulting dark brown complex was filtered and washed several times with distilled water at 80°C and

hexane at 55°C. Then, the complex was dried in air for 48 h.

FTIR Study of the Samples

The FTIR spectra of the samples were recorded using a Nicolet Protege 460 spectrometer in the range 4000–400 cm^{-1} using a transmittance procedure with a resolution of 4 cm^{-1}. The spectra were processed with the OMNIC® program. The computer treatment of the spectra included smoothing of the spectrum and background subtraction. Dry particles of palladium complexes with the initial and modified chitosan, as well as the initial polymers themselves, were ground in a mortar, and the resulting highly dispersed powder was mixed with KBr. The mixture was pressed to obtain thin pellets and placed in a Nicolet spectrometer cell.

XPS Study of the Catalysts

The catalysts were studied by the XPS method using an XSAM-800 (Kratos) spectrometer with $AlK_{\alpha_{1,2}}$ irradiation. The atomic ratios were determined from the integral intensities of the peaks using the cross-sections of photoionization for $AlK_{\alpha_{1,2}}$ irradiation. The binding energies were corrected taking into account sample charging, using the C 1s line (285.0 eV) as a reference.

Experimental Modeling of Catalytic Steps of Hexene-1 and Heptene-1 Oxidation

The reaction was carried out in a periodic constant-temperature reactor equipped with a magnetic stirrer and a sampler.

The reaction conditions were as follows: the olefin concentration was 0.03–0.06 mol/l; a 0.1–0.05 M aqueous solution of HCl was used as a solvent; the oxidant was O_2; the reoxidation system was H_2O_2, H^+ (the concentration of hydrogen peroxide was varied from 0.1 to 0.5 mol/l); the reaction time was 8–15 h; the temperature was 25°C; and the substrate/catalyst ratio was 10/1–20/1.

The concentration of palladium in the catalysts based on chitosan modified by a glutaric aldehyde was 1 wt %.

The catalytic steps of hexane-1 and heptane-1 oxidation consisted of carrying out the reactions in stages: (1) the interaction of the palladium complex with an olefin and (2) the regeneration of the spent complex by the reoxidation system.

Products were analyzed by gas chromatography using a Model 3700 chromatograph equipped with a flame ionization detector and a 4-m column with an inner diameter of 4 mm. The column was packed with 5% SE 31 on inerton AW.

RESULTS AND DISCUSSION

IR spectroscopic study of complexes. The IR spectra of all samples are characterized by the presence of absorption bands of chitosan and its derivatives: (1) broad unstructured absorption in the range 3700–3100 cm^{-1}, related to the superposition of the stretching vibrations of OH and NH groups; (2) narrow bands of stretching vibrations of CH groups in the range 2800–3000 cm^{-1}, related to CH_2 (2860 and 2930 cm^{-1}) and CH (~2900 cm^{-1}) groups; (3) the bands of deformational vibrations in the NH group in the range 1660–1530 cm^{-1}; and (4) the bands of deformational vibrations of C–O groups in ether fragments at 1712 cm^{-1} [18].

Nonmodified chitosan. Compared to the spectrum of the initial polymer (Fig. 1), in the IR spectra of palladium complexes of nonmodified (initial) chitosan prepared by two different methods a decrease in the relative intensity of the bands of deformational vibrations of the N–H bond in the range 1630–1550 cm^{-1} is observed. It is noteworthy that the spectra of palladium complexes contain intense bands in the region of low frequencies, which can be assigned to the stretching vibrations of Pd–N and Pd–O bonds (450–550 cm^{-1}).

Palladium chitosan complex prepared by the adsorption method. For the complex obtained by the adsorption (impregnation) method, this band is observed at 474 cm^{-1}, which agrees with the literature data for the ammonia complex $[Pd(NH_3)_2Cl_2]$ [20], for which the stretching frequency of the Pd–N bond is 476 cm^{-1} (Fig. 1).

Because palladium chloride was used in the preparation of the complex and because the presence of chlorine is confirmed by elemental analysis, one may assume that the structure $[Pd(RNH_2)_2Cl_2]$ can be valid for the case of adsorption complexes. In such a structure the coordination is as in the comlex mentioned above, where halide ligands and ligands donated by chitosan are monodentate (Fig. 2a).

Palladium chitosan complex prepared by the coprecipitation method. In the complex obtained by the coprecipitation chitasanium hydrochloride and the tetrachloropalladate ion, the band of stretching vibrations of the Pd–N bond shifts toward higher frequencies and the structure of this band becomes more complex (555 and 606 cm^{-1}). An increase in the frequency points to the formation of a stronger Pd–N bond. The stretching of the Pd–O bond are likely to contribute to the structure of the complex band for the complex obtained by the coprecipitation method.

Furthermore, a change in the region of deformational vibrations of the hydroxy groups of chitosan (1300–1400 cm^{-1}) suggests additional coordination of the metal to the OH group of the polysaccharide via the oxygen atom. In the case of coprecipitation, halide atoms are removed by treatment in alkali in the course of preparation, and the ligand environment of palladium only consists of the ligands of the polymeric
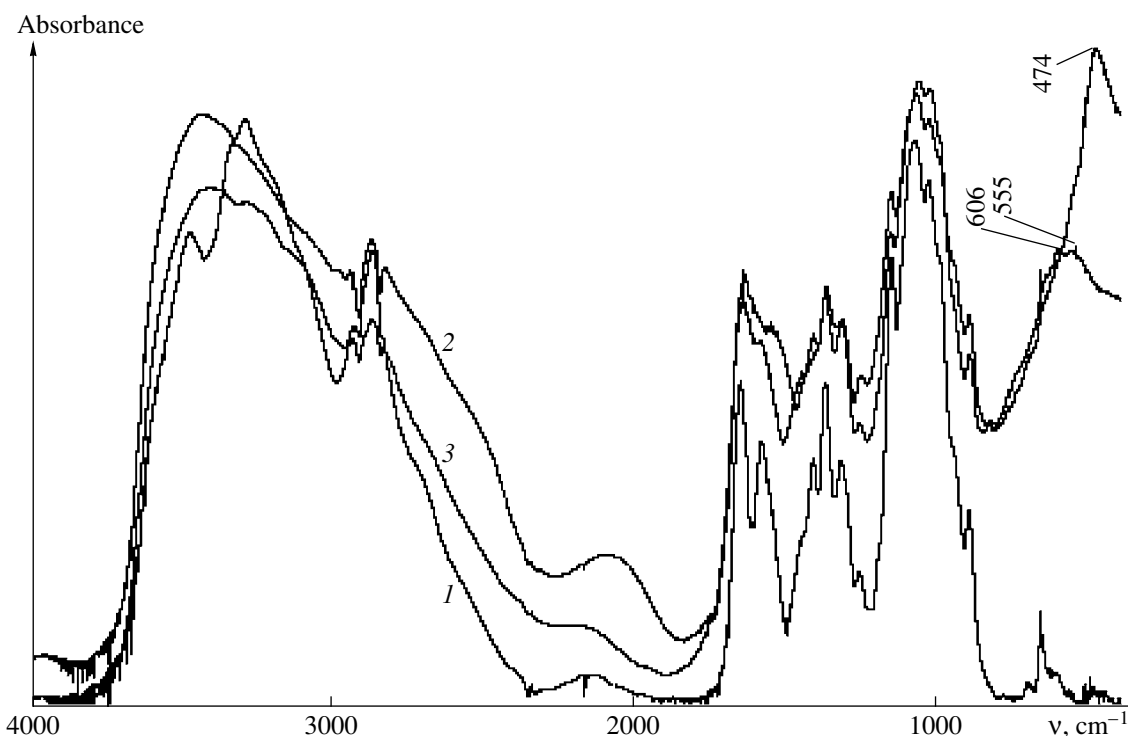
Absorbance

Fig. 1. IR spectra of (*1*) initial chitosan and its complexes with palladium obtained by the method of (*2*) adsorption and (*3*) coprecipitation.
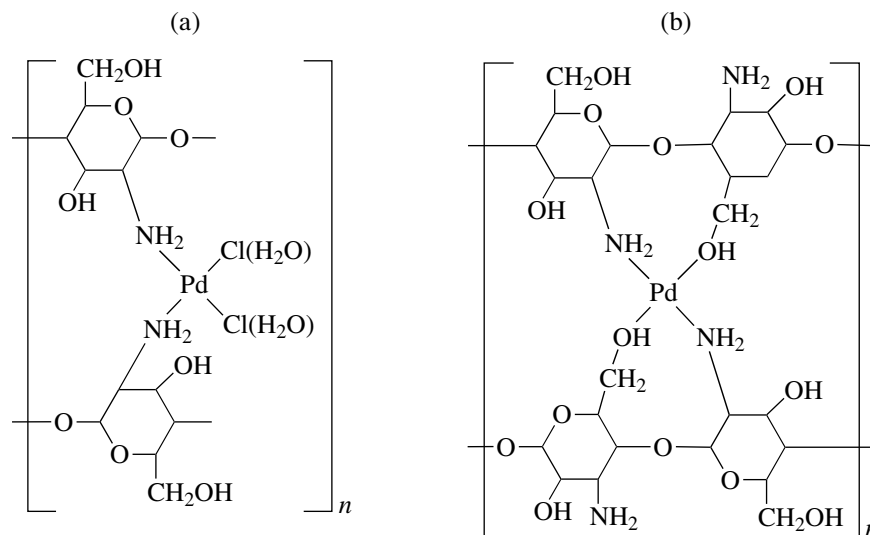

Fig. 2. Proposed structure of the Pd(II) complex with chitosan: (a) adsorption and (b) coprecipitation.

matrix. The most stable structure would be the one with chelating or bidentate ligands. Neighboring chitosan rings may serve as such chelating ligands. Bonding to the central atom in such ligands would be via the nitrogen atoms of amino groups or via the oxygen atoms of hydroxy groups. The intermediate variant is the most probable, wherein one chitosan ring provides a nitrogen atom and another ring provides an oxygen atom (Fig. 2b). This is due to the spatial structure of chitosan,

in which the amino groups of neighboring rings cannot belong to a single plane [20].

These conclusions agree well with DFT calculations [21] of the simplest chitosan complexes of metals with oxidation state 2+. It was found that the minimum-energy structures are chelates shown in Fig. 3.

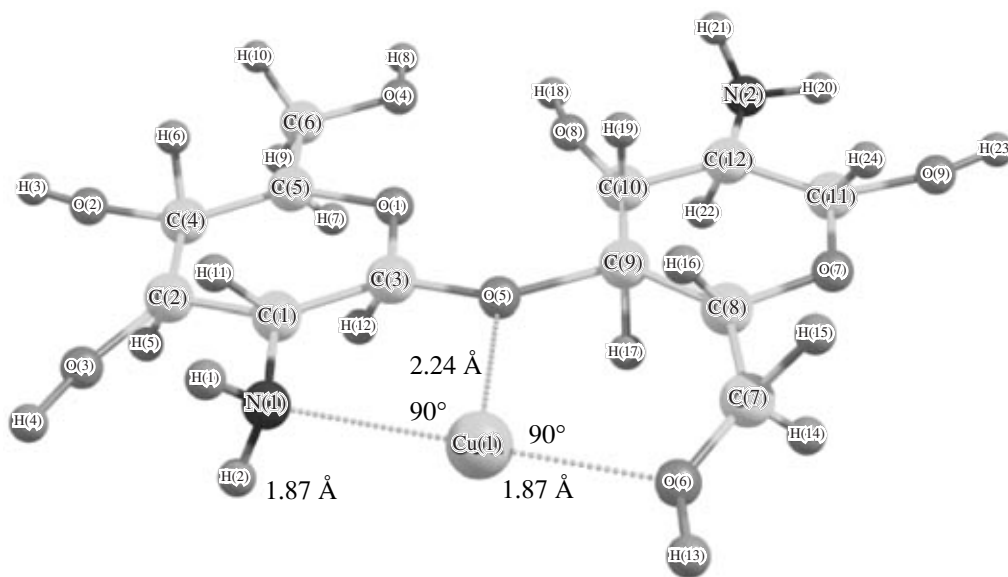Thus, in the case of the adsorption method, the complex is formed by ligand exchange and has the hypo-

Fig. 3. Optimized structure of chitosan disaccharide complex with Cu(II).

thetical structure [Pd(RNH$_2$)$_2$Cl$_2$]. In the case of coprecipitation, chelate complexes are the most probable, with coordination of the amino and hydroxy groups of neighboring chitosan rings to a palladium atom. Metal chelating by amino groups of chitosan rings from different polymer chains is also possible.

Chitosan modified by glutaric aldehyde. Upon modification of initial chitosan with glutaric aldehyde (by the Schiff reaction), the IR spectrum contains a band with a maximum at 1712 cm^{-1}, which corresponds to the stretching vibrations of the free carbonyl group of glutaric aldehyde (Fig. 4). A spectral pattern observed for the complexes of the initial polymer is generally reproduced for the palladium complexes with the modified polymer (Fig. 4). In the complex prepared by adsorption of the tetrachloropalladate ion on the polymer surface, a change in the relative intensity of the bands in the region of deformational vibrations of the N–H bond is accompanied by the appearance of an intense band in the region of low frequencies (the absorption maximum is at 474 cm^{-1}). This band can be assigned to the stretching vibrations of the Pd–N bond.

For the template complex (Fig. 5), broadened, poorly resolved bands with absorbance maxima at 474 and 555 cm^{-1} are observed. They point to the presence of coordination of two types. In the course of template preparation, at the stage of interaction of glutaric aldehyde with the homogeneous palladium complex with chitosan, the metal may partly be reduced. To determine the contribution of Pd(0) to the spectral pattern, the complex was additionally reduced by NaBH$_4$. In the spectrum of the additionally reduced template complex, the band with a maximum at 555 cm^{-1} shifts to 621 cm^{-1}, a value that probably corresponds to the
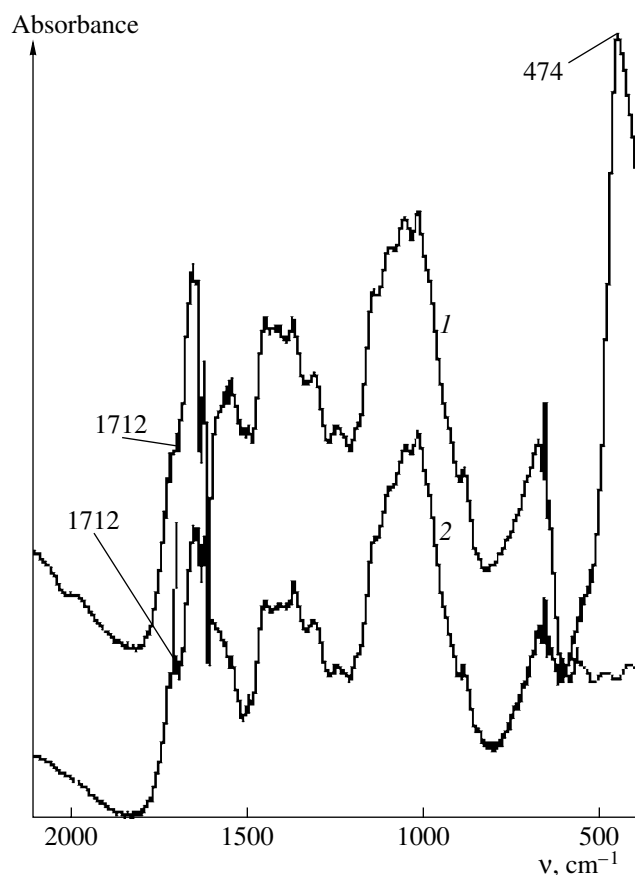
Fig. 4. IR spectra of (*1*) chitosan modified by the glutaric aldehyde and (*2*) the palladium complex with chitosan modified by glutaric aldehyde obtained by the adsorption method.

vibrations of the Pd(0)–N bond, whereas the band at 474 cm^{-1} is preserved. The regeneration of the template complex by hydrogen peroxide both after preparation and after additional reduction by NaBH$_4$ leads to a drastic increase in the intensity of the band at 474 cm^{-1}, but the low-intensity band at 555 cm^{-1} is preserved.

Study of the Complexes in the Reaction of Olefin Oxidation

The catalysts obtained were studied in the oxidation of hexane-1 and heptene-1. Since chitosan complexes are soluble in dilute acids, catalysts based on nonmodified chitosan were tested in a neutral medium. GC analysis of the reaction mixtures allowed us to determine that, in the case of the sample obtained by coprecipitation, the only reaction route is isomerization into hexene-2 and hexene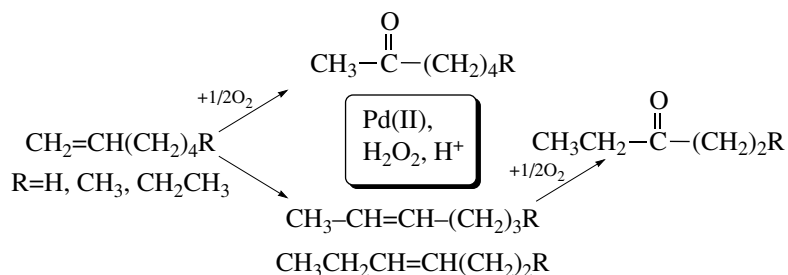-3. Oxidation products were not observed. If the complex was prepared by adsorption, oxidation products were found, but the conversion of olefin was very low. This is probably due to the fact that some initial acidic background is needed to initiate the reaction in the homogeneous process, in addition to the acid formed at the first stage of oxidation.

Complexes of chitosan modified by glutaric aldehyde were tested in a medium of 0.05 M HCl. In the course of the reaction, we detected the formation of products of olefin isomerization, but the products of oxidation dominated (see Scheme).

Separate stages of the catalytic oxidation of hexane-1 were studied:

Stage 1: Catalyst interaction with an olefin without reoxidation.

Stage 2: Catalyst treatment with the reoxidant.

$$CH_3-\overset{\overset{\textstyle O}{\|}}{C}-(CH_2)_4R$$

$$+1/2O_2$$

$$CH_2=CH(CH_2)_4R$$

$$R=H, CH_3, CH_2CH_3$$

Pd(II), H$_2$O$_2$, H$^+$

$$CH_3CH_2-\overset{\overset{\textstyle O}{\|}}{C}-(CH_2)_2R$$

$$+1/2O_2$$

$$CH_3-CH=CH-(CH_2)_3R$$

$$CH_3CH_2CH=CH(CH_2)_2R$$

Reaction conditions: Solvent, H$_2$O, Substrate/catalyst = 10/1,

τ = 8 h, [HCl] = 0.05 M

Scheme. Oxidation of terminal olefins.

The reoxidant was 0.5 M H$_2$O$_2$ in an acidic medium (0.05 M HCl). The catalyst sample, after treatment with olefin, changes its color from yellow to dark grey. IR spectra were obtained for the adsorbed complex (Fig. 6). In the range 1650–1400 cm^{-1}, a series of narrow bands with complex structures were observed. In our opinion, there may be several reasons for this: first, the olefin might be incompletely removed from the catalyst, and the appearance of intense bands at 1616–1639 cm^{-1} corresponds to the stretching vibrations of the C=C bond in the olefin; second, the olefin may be coordinated to the metal atom, because it is known that homogeneous oxidation occurs via the formation of olefin π-complexes. Changes in the relative intensities of the bands in the region of deformational vibrations of hydroxy groups of the complex (1300–1400 cm^{-1}) may also point to the formation of an intermediate species.

A band corresponding to the stretching vibrations of the Pd–N bond, which was observed in the spectrum of the initial catalyst at 470 cm^{-1}, shifts toward higher frequencies and splits into two bands (621 and 532 cm^{-1}). This is likely to be due to the fact that, in the course of palladium reduction, direct reduction (621 cm^{-1}) is accompanied by a change in the coordination of a portion of monodentate Pd(II) to the chelate form (532 cm^{-1}).

Upon catalyst regeneration, the spectrum contains the same series of bands at 1650–1400 cm^{-1} as does the complex before a catalytic reaction. The low-frequency region contains two broadened bands of moderate intensity (at 555 and 470 cm^{-1}). These correspond to the vibrations of the Pd–N bonds in chelate and monodentate structures.

XPS Study

The XPS method was used to study the charge state of the metal in the course of catalytic transformations. The XPS spectrum of the initial adsorbed palladium complex with chitosan modified by the glutaric aldehyde contains a signal corresponding to Pd(II) only (E_bPd3$d_{5/2}$ = 337.8 eV) (Fig. 7). Upon interaction with the olefin, the spectrum of the sample contains both the signal from Pd(II) (E_bPd3$d_{5/2}$ = 337.8 eV) and from Pd(0) (E_bPd3$d_{5/2}$ = 335.7 eV). The spectrum of the complex, upon regeneration with hydrogen peroxide, again shows the signal from Pd(II), but the binding energy shifts toward lower energies (E_bPd3$d_{5/2}$ = 337 eV). This

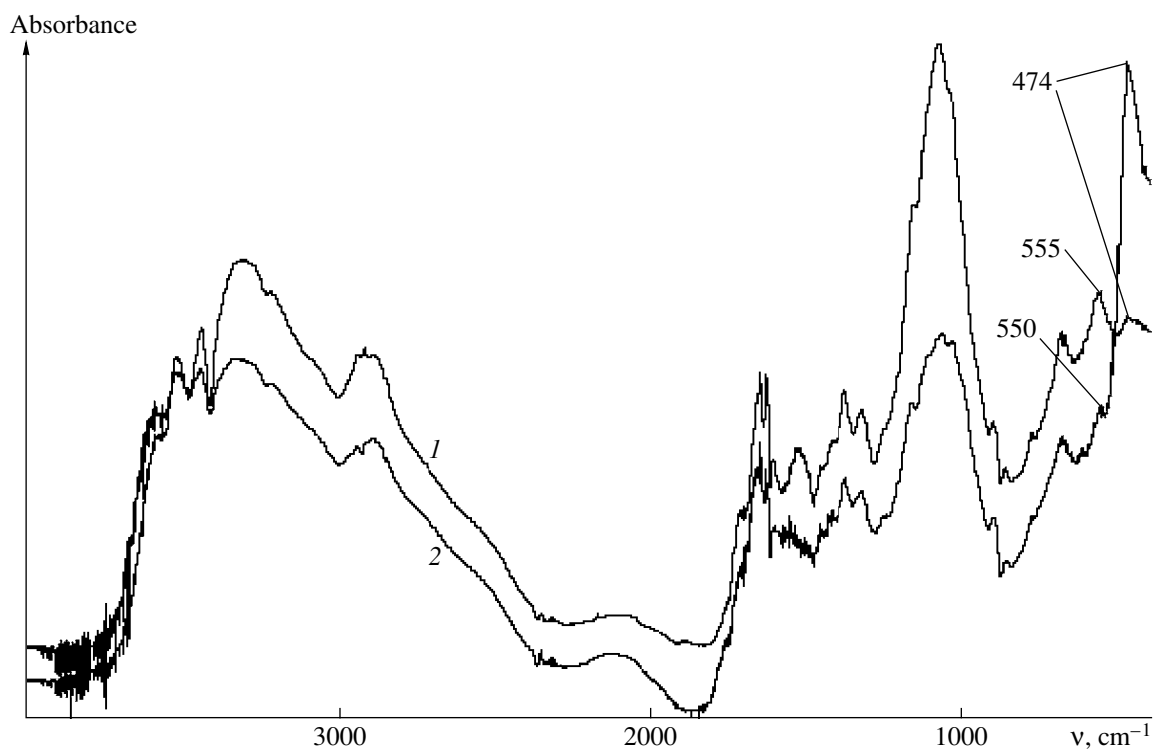**Fig. 5.** IR spectra of the template complex of palladium with chitosan modified by glutaric aldehyde (*1*) before and (*2*) after regeneration with H_2O_2.
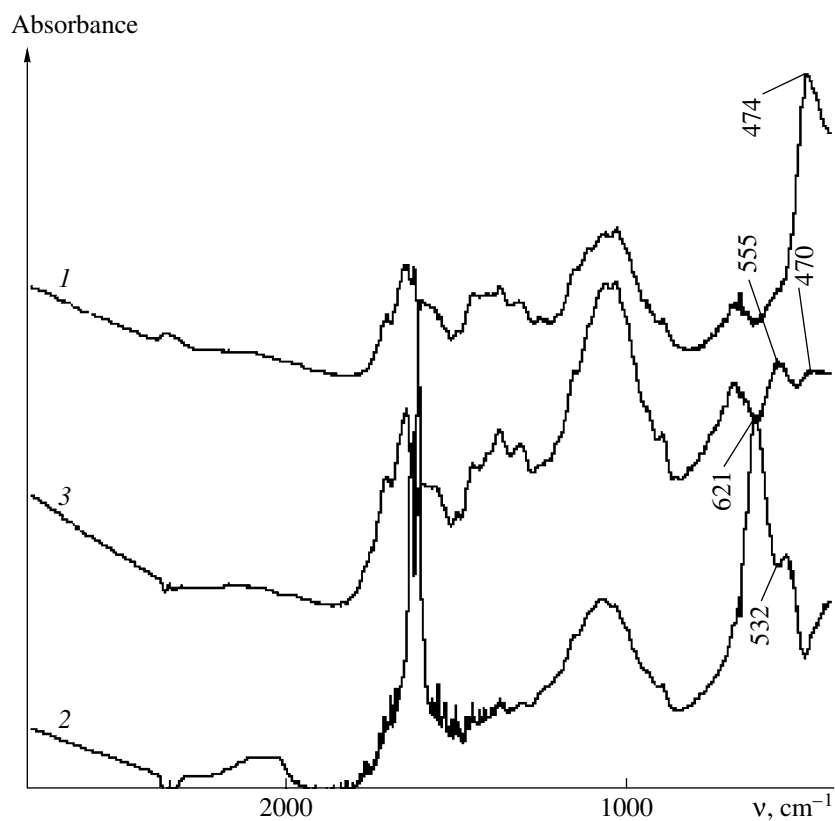

Fig. 6. IR spectra of palladium complexes at different stages of olefin oxidation: (*1*) Pd complex with chitosan modified by glutaric aldehyde obtained by the adsorption method; (*2*) after interaction with the olefin; and (*3*) after regeneration with H_2O_2.
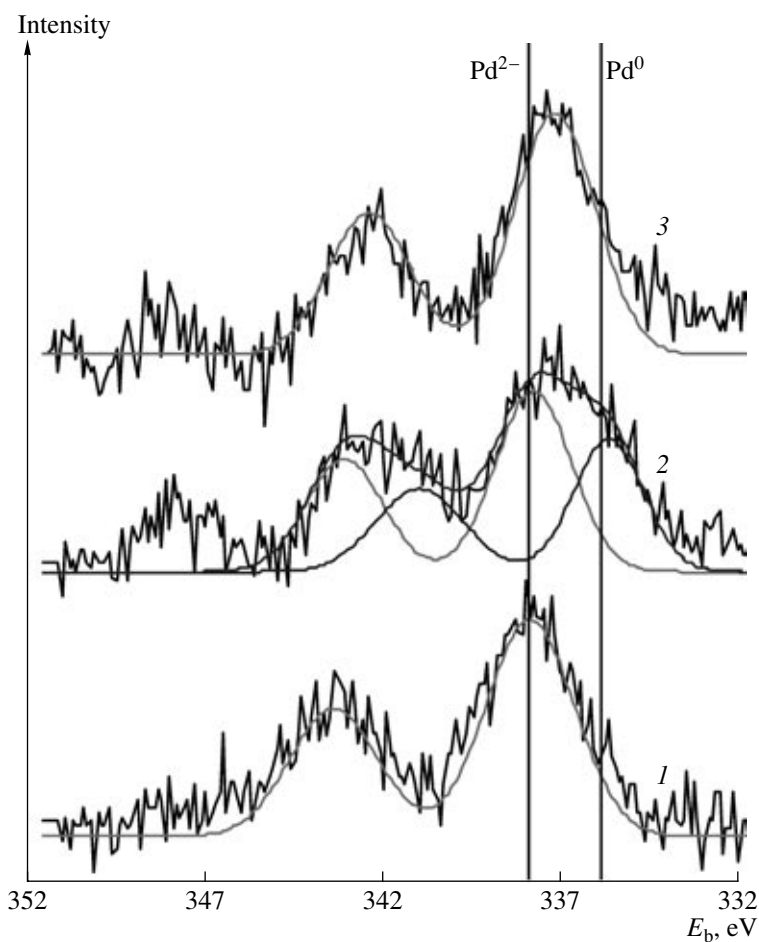
Intensity

Fig. 7. XPS spectra of palladium complexes at different stages of olefin oxidation: (*1*) Pd complex with chitosan; (*2*) after interaction with the olefin; and (*3*) after regeneration with H_2O_2.

points to a change in the ligand environment of palladium. Probably, the number of ligands of the central atom increases. This assumption does not contradict a partial change of the monodentate coordination to the chelating one [21]. Thus, the XPS data agree with the results obtained by FTIR spectroscopy: upon regeneration, the FTIR spectrum contains two bands (470 and 555 cm^{-1}) that supposedly correspond to monodentate and chelate palladium.

CONCLUSIONS

1. In the case of the adsorption complex of the modified polymer and initial chitosan, the dominating form of palladium coordination is monodentate binding via the amino group of the glycoside ring.

2. In the case of the template palladium complex, coordination may be of two types: monodentate binding and chelating. In the case of a complex with nonmodified chitosan obtained by coprecipitation, the main type of coordination is chelating.

3. Redox transformations may alter coordination (chelate fragments become monodentate-bound, and vice versa).

4. The complexes may undergo redox transformations without changing their structure and without metal transfer to the reaction medium.

5. The use of heterogenized palladium complexes as catalysts for the oxidation of terminal olefins leads to the formation of oxidation and isomerization products, as in the case of homogeneous oxidation.

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