

# Heterogenized palladium chitosan complexes as potential catalysts in oxidation reactions: study of the structure

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Received 29 May 2003; received in revised form 6 August 2003; accepted 9 August 2003

## Abstract

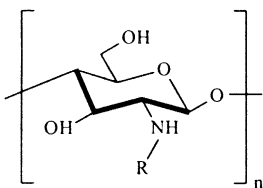
Complexes of palladium with chitosan were prepared by different methods such as coprecipitation and adsorption and studied by EXAFS, FTIR, and X-ray photoelectron spectroscopy (XPS). It was found in the case of the coprecipitation-type complex that a chelate structure is a likely state of palladium. In the case of the adsorption-type system, palladium is coordinated by two chitosan NH<sub>2</sub> groups without chelation. It is evident from the EXAFS and XPS data that the structure of the complexes changes in the course of palladium reduction. In the case of the complex prepared by coprecipitation, Pd(0) atoms presumably form trimers in a polymer matrix; the formation of dimeric structures seems to be most typical of the adsorption complex. XPS data show the possibility of reversible redox transformations of palladium immobilized on a chitosan matrix. The complexes prepared can be considered as potential oxidation catalysts.

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**Keywords:** Chitosan; Pd(II) immobilization; Heterogenized catalysts; Oxidation; EXAFS; FTIR; XPS

## 1. Introduction

Immobilization of transition metal complexes on the surface of polymer supports allows to design new catalysts that combine the advantages of homogeneous and heterogeneous catalytic systems. Recently, organic polymers including natural materials (such as cellulose, chitin, and chitosan) are being considered as promising carriers for immobilized complexes.



These systems are ecologically friendly materials meeting the needs for catalysts of a new generation. The unique properties of natural polymers, such as biodegradability, blood compatibility, etc. make them especially attractive for a number of potential applications [1–3].

Chitosan (poly(1-4)-*N*-acetyl-β-D-glucosamine) extracted by deacetylation of chitin, a component of crab shells, insects, and plant cell walls is one of the most abundant natural polysaccharides. There exist unlimited resources of chitosan-rich unused crab shells which cause worrisome environmental problems.

Presently, diverse applications of chitosan are being launched into a commercial stage. For chitosan and its derivatives, the term “compounds of the XXI century” has been coined. There are some strong grounds to believe that this is true [4–6]:

- (i) Chitosan exhibits perfect compatibility with vital organism media.
- (ii) It is characterized by a high nitrogen content, which explains, in turn, its ability to concentrate metal ions

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and even neutral atoms of different metals via different mechanisms such as ion exchange or chelate formation, depending on the metal and pH of the solution.

Taking into account the unique properties of chitosan, one can indicate some potential advantages of this polymer as a carrier for the heterogenization of metal complexes:

- (1) Presence of different functional groups.
- (2) Easy modification and even possibility to use it without preliminary modification.
- (3) High metal dispersion on the surface of a chitosan support.
- (4) Rather high thermal stability, durability.
- (5) Easy recovery of valuable components from the catalysts by incineration and metal extraction.

Thus, chitosan could be considered as a promising carrier for the immobilization of metal complexes, and heterogenized metal complexes fixed on the surface of chitosan are good candidates to be “green catalysts”. However, surprisingly, only a few publications focused on the application of chitosan-supported metal complexes in heterogeneous catalytic processes are available in the open literature, and the structure of these macroligand complexes is insufficiently characterized (e.g., *ab initio* calculations [7]).

Chitin and chitosan complexes with platinum group metals are used in heterogeneous catalytic hydrogenation reactions (including asymmetrical hydrogenation) [8,9].

Rare earth metal–chitosan complexes are employed as catalysts in polymerization reactions (substrates: ethylene oxide, propylene oxide, methyl methacrylate, and epichlorohydrin) [10]. Immobilization of different enzymes (protease, oxidase) on chitin and chitosan supports increases their stability and efficiency [11]. Data concerning heterogeneous catalytic oxidation with metal complexes immobilized on chitosan are absent. There is some information on diphenol and catecholamine oxidation with iron and cobalt complexes with chitosan derivatives [12,13]. However, all these processes are homogeneous. Recently, the heterogenized copper complexes were used as catalysts in the oxidation of isomeric dihydroxybenzenes [14].

As we found in above-mentioned paper that the chitosan matrix can retain copper ions that undergo redox transformations [14]. The same type of palladium complexes can also be considered as potential heterogenized catalysts. It is well known that oxidation of terminal olefins (Wacker-type oxidation) in aqueous solutions proceeds in the presence of palladium(II) salts [1,15,16]. Hence, palladium–chitosan complexes are good candidates for catalytic applications. Furthermore, heterogenization of such complexes can make the catalytic systems cost-effective, while retaining the specific advantages of the homogeneous metal complexes, such as high activity and selectivity, after their heterogenization.

Thus, the goals of this study were to design a heterogenized palladium complex possessing the properties of an oxidation catalyst and to characterize its structure. This complex should undergo redox reactions in aqueous solutions without degradation of the complex structure.

## 2. Experimental

### 2.1. Materials

As-received chitosan powder (made in Korea from crab shells, molecular weight 100,000–150,000) was used without further purification. The deacetylation degree of amino groups was 70%, the moisture content in the chitosan powder was 3 wt.%. PdCl<sub>2</sub> was purchased from Fluka AG (Switzerland) as an analytical grade reagent, HCl and NaOH were also of analytical grade purity.

### 2.2. Complex preparation

Chitosan was modified with palladium by different methods such as adsorption of PdCl<sub>4</sub><sup>2-</sup> from neutral solutions on the surface of chitosan or coprecipitation of a soluble form of chitosan with divalent palladium precursors. The metal content varied from 1 to 5 wt.% (a Pd content of 5 wt.% was chosen for the adsorption complex in order to intensify and clarify possible metal–metal interactions on the surface of chitosan).

#### 2.2.1. Homogeneous palladium–chitosan complex (starting material for the heterogenized complexes)

A calculated amount of PdCl<sub>2</sub> was added to a 1.5 wt.% solution of chitosan in 0.1 M HCl at room temperature, and the mixture was stirred until the formation of a yellow clear solution.

#### 2.2.2. Coprecipitation method

A yellow clear solution of the homogeneous palladium–chitosan complex (1% Pd–chitosan) was prepared as described above and added dropwise to a glass beaker with a 0.5 M NaOH solution, which led to immediate coagulation of the drops into spherical globules. The spherical particles formed (diameter, 2–3 mm) were filtered off after 10 min and repeatedly washed with distilled water until neutral pH. After this procedure, the globules of chitosan containing immobilized palladium were filtered off and air-dried at room temperature for 48 h.

#### 2.2.3. Adsorption method

A 1.5 wt.% chitosan solution was added dropwise to a glass beaker with a 0.5 M NaOH solution, which resulted in immediate formation of spherical globules of pure chitosan. The particles were filtered off after 10 min, repeatedly washed with distilled water until neutral pH, filtered again, and air-dried at room temperature for 48 h. A weighed

amount of palladium chloride (to achieve a composition of 5% Pd–chitosan—quantitative adsorption of Pd<sup>2+</sup> assumed) was dissolved in 20 ml of distilled water and stirred with 1.0 g of dried chitosan particles for 20 min. Then the particles were removed by filtration, washed with distilled water and air-dried for 24 h.

The Pd–chitosan complexes were studied in the as-received form, after reduction with NaBH<sub>4</sub> and after reoxidation with H<sub>2</sub>O<sub>2</sub>. For the reduction, the Pd–chitosan sample were suspended in water (5 ml per 1 g of granules), and a calculated amount of NaBH<sub>4</sub> (molar ratio Pd:NaBH<sub>4</sub> = 1:1) was added. The Pd–chitosan granules were stirred in the NaBH<sub>4</sub> solution until the hydrogen evolution stopped. The dark grey reduced samples were filtered and air-dried for 24 h.

For the reoxidation reduced Pd–chitosan samples were suspended in water (5 ml per 1 g of granules) and treated with a calculated amount of 10% hydrogen peroxide for 8 h, until the complexes color became light yellow. The regenerated samples were filtered off and air-dried for 24 h.

### 2.3. Characterization

The Pd–chitosan complexes were characterized by elemental analysis, EXAFS, IR spectroscopy, and X-ray photoelectron spectroscopy. XRD analysis was not possible because the materials proved to be X-ray amorphous.

#### 2.3.1. IR spectroscopy

Transmission FTIR spectra were recorded at 20 °C using a Nicolet Protege 460 spectrometer in the range of 4000–400 cm<sup>-1</sup> at a resolution of 8 cm<sup>-1</sup>, and also with a Matteson Galaxy Series FTIR 5000 spectrometer in the range of 4000–600 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. For the study of the homogeneous palladium–chitosan complex, some droplets of the solution were deposited on quartz plates and air-dried for 48 h. Dry globules of heterogeneous chitosan samples (adsorption and coprecipitation complexes) were ground in a mortar, the fine powder was mixed with KBr, pressed into a thin pellet, and placed in the sample

holder of the spectrometer. The OMNIC software was used for the processing of the spectra.

#### 2.3.2. EXAFS

EXAFS measurements were carried out at HASYLAB (DESY in Hamburg, Germany) on the beamline X1 using a double-crystal Si(3 1 1) monochromator. The energy resolution was estimated from the angular beam size to be 7.1 eV (standard deviation) at the Pd K-edge (24350 eV). The XAFS spectra were recorded in the transmission mode at low temperature (*T* = 80 K) in order to decrease the Debye–Waller factors. To extract quantitative information from EXAFS spectra, Fourier-filtered shell contributions were fitted using the standard EXAFS formula in the harmonic approximation:

$$\chi = S_0^2 \sum_j \frac{N_j F_j(k)}{k R_j^2} \exp(-2\sigma_j^2 k^2) \sin[2kR_j + \phi_j(k)]$$

with the summation over atomic shells *j*. The required scattering amplitudes and phase shifts *F* and  $\phi$  were calculated by the ab initio FEFF8.10 code [17]. The fitting was done in *k*- and *r*-spaces. The shell radius *R<sub>j</sub>*, coordination number *N<sub>j</sub>*, Debye–Waller factor  $\sigma_j^2$ , and adjustable ‘muffin-tin zero’  $\Delta E_j$  were determined as fitting parameters. The multiple-excitation reduction factor *S*<sub>0</sub><sup>2</sup> was used as calculated by the FEFF8.10 code (*S*<sub>0</sub><sup>2</sup>(Pd) = 0.923). The errors of the fitting parameters were found via decomposition of the statistical  $\chi^2$  function near its minimum taking into account maximal pair correlations. The analysis of the EXAFS spectra was performed with the software VIPER for Windows [18].

When using calculated scattering amplitudes and phase shifts (*F*,  $\phi$ ), it is necessary to test their reliability with a reference material. The results of such a test with a PdO reference are summarized in Fig. 1 and Table 1. The crystallographic Pd–O and Pd–Pd distances given in the table were derived from literature data, which refer to room temperature ([19], PdO: *P4*<sub>2</sub>/*mmc*; *a* = 3.03 ± 0.01; *c* = 5.33 ± 0.02;

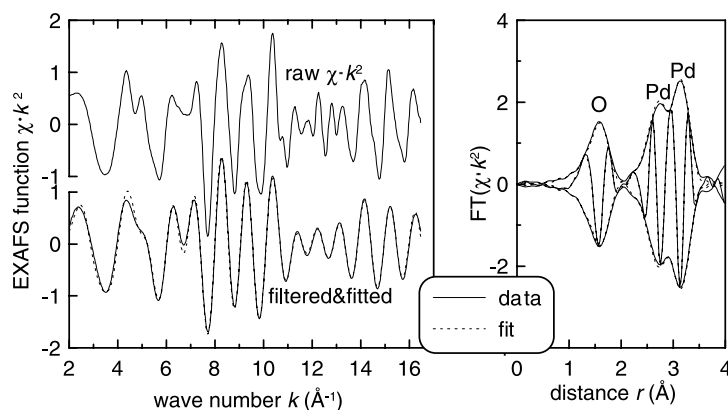


Fig. 1. Analysis of EXAFS spectra for the reference material PdO.

Table 1

Comparison of model parameters derived from the EXAFS spectrum of PdO shown in Fig. 1 with crystallographic data [9]

Bond	$R$ (Å)	$R_{\text{cryst}}^a$ (Å)	CN	$\text{CN}_{\text{cryst}}$	$\sigma^2$ ( $\times 10^{-3}$ Å <sup>2</sup> )	$\Delta E$ (eV)
Pd–O	2.03 (1)	2.018	4.0 (3)	4	3 (1)	11 (1)
Pd–Pd	3.037 (5)	3.030	4.0 (6)	4	3.1 (8)	5.8 (8)
	3.428 (6)	3.419	7.9 (9)	8	3.9 (7)	

The standard errors in the last digit are given in parentheses. EXAFS data refer to 80 K.

<sup>a</sup> At room temperature.

$\text{Pd}_1 = 0, 0, 0$ ;  $\text{Pd}_2 = 0.5, 0.5, 0.5$ ;  $\text{O}_1 = 0.5, 0, 0.25$ ;  $\text{O}_2 = 0.5, 0, 0.75$ ). The good reproduction of the experimental spectrum achieved by a fit with realistic distances and coordination numbers (Table 1) shows that the calculated amplitude and phase-shift data are reliable. No extra broadening by adding an ad hoc imaginary part into the exchange-correlation potential) in the FEFF calculation was required to achieve such a good coincidence.

### 2.3.3. XPS

An X-ray photoelectron spectroscopy (XPS) study of the palladium–chitosan complexes was carried out using an XSAM-800 (Kratos) spectrometer with Al  $K\alpha_{1,2}$  irradiation. The atomic ratios were determined from the integral peak intensities by using the photoionization cross-sections for Al  $K\alpha_{1,2}$  radiation [20]. The binding energies ( $E_b$ ) were corrected to take into account the effect of sample charging using the C 1s signal (285.0 eV) as a standard.

## 3. Results

### 3.1. Adsorption complex

#### 3.1.1. IR spectroscopy

The IR spectra of all samples studied are characterized by the absorption bands of chitosan and its derivatives (Fig. 2, lower curve): (1) a broad unstructured absorption between 3700 and 3100  $\text{cm}^{-1}$  related to the superposition of OH and NH group stretching vibrations; (2) narrow bands of CH group stretching vibrations at 2800–3000  $\text{cm}^{-1}$ , assigned to  $\text{CH}_2$  (2860 and 2930  $\text{cm}^{-1}$ ) and CH ( $\sim 2900$   $\text{cm}^{-1}$ ) fragments; and (3) bands of deformational NH group vibrations of in the 1660–1530  $\text{cm}^{-1}$  range [21,22]. Additionally, the IR spectra of Pd–chitosan complexes prepared by different methods exhibits an intense set of bands in the low-frequency region (650–400  $\text{cm}^{-1}$ ). Preliminarily, these bands are ascribed to stretching vibrations of Pd–N, Pd–O bonds.

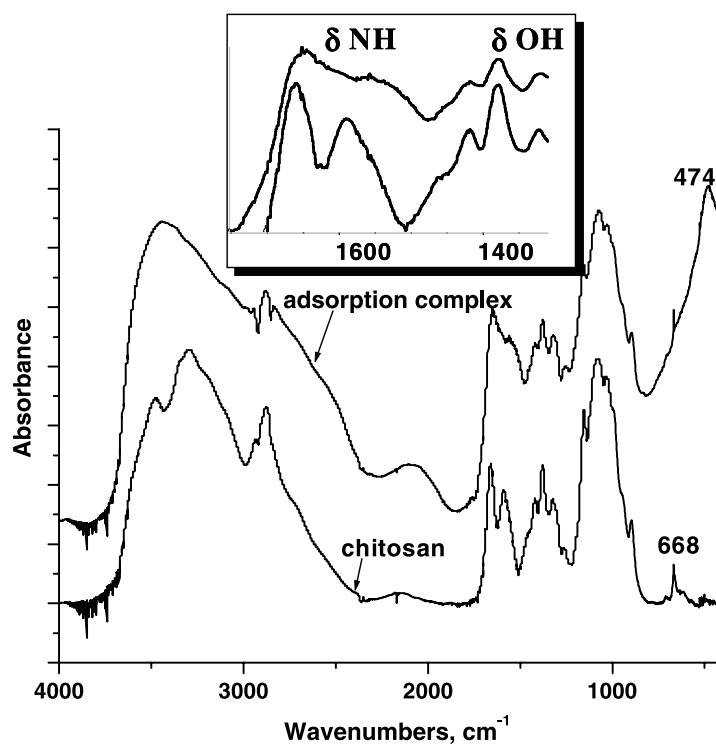


Fig. 2. IR-spectra of initial chitosan and of chitosan modified with palladium by adsorption of  $\text{PdCl}_2$  from aqueous solution.

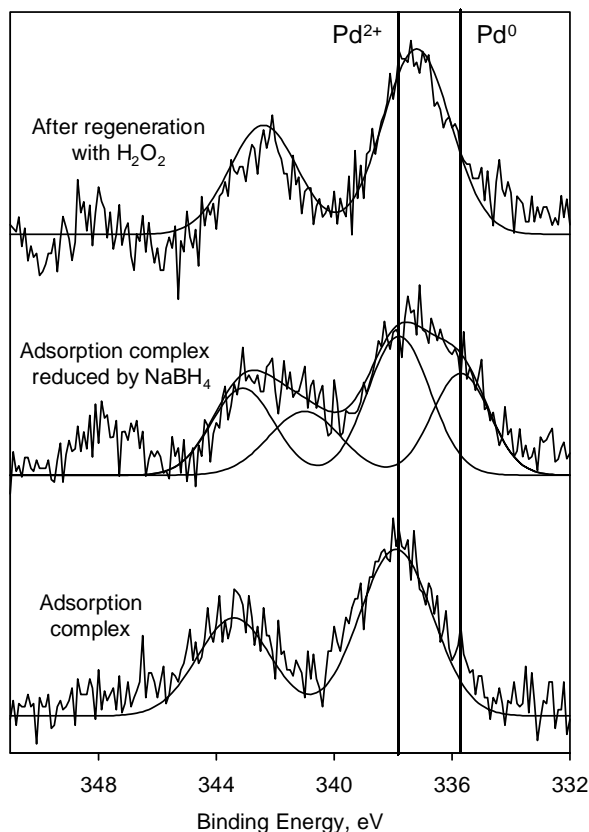


Fig. 3. Pd 3d XP spectra of the adsorption complex between palladium and chitosan after preparation, reduction with  $\text{NaBH}_4$  and reoxidation with  $\text{H}_2\text{O}_2$ .

With the adsorption complex, this set of bands is observed as a broad feature peaking at  $474\text{ cm}^{-1}$  (Fig. 2). Furthermore, there is also a change in relative intensities in the region of deformational NH group vibrations ( $1500\text{--}1680\text{ cm}^{-1}$ ).

### 3.1.2. XPS

Pd 3d XP spectra of the adsorption complex in the as-prepared form, after reduction with  $\text{NaBH}_4$  and reoxida-

Table 2

EXAFS results for the adsorption complex between palladium and chitosan: model parameters

Sample	Bond	$R$ (Å)	CN	$\sigma^2$ ( $10^{-3}\text{ Å}^2$ )	$\Delta E$ (eV)
As-prepared	Pd–O <sup>a</sup>	2.04 (1)	2.4 (2)	1 (1)	20 (1)
	Pd–O <sup>a</sup>	2.18 (2)	1.8 (2)	1 (2)	
Reduced	Pd–O <sup>a</sup>	2.031 (7)	2.8 (1)	4 (1)	14 (1)
	Pd–Pd	2.78 (3)	1.2 (3)	10 (4)	10 (3)

Values shown in parentheses are the standard errors.

<sup>a</sup> Light element, O or N, Cl not excluded.

tion with  $\text{H}_2\text{O}_2$  are displayed in Fig. 3. The spectrum of the initial palladium–chitosan adsorption complex exhibits a signal characterized by  $E_b$  (Pd  $3d_{5/2}$ ) = 337.8 eV (Fig. 2). Reduction of the sample with  $\text{NaBH}_4$  lead to significant changes in the signal shape, which can be fitted by two doublet contributions. One of the doublets has the same binding energy as the original signal ( $E_b$  (Pd  $3d_{5/2}$ ) = 337.8 eV) whereas the other one is typical of metallic palladium ( $E_b$  (Pd  $3d_{5/2}$ ) = 335.7 eV). After reoxidation with  $\text{H}_2\text{O}_2$ , the initial signal was restored in shape and intensity, however, the binding energy was shifted to lower values and became  $E_b$  (Pd  $3d_{5/2}$ ) = 337.0 eV.

### 3.1.3. EXAFS

The EXAFS spectra of the adsorption complex in the as-prepared form and after reduction with  $\text{NaBH}_4$  are displayed in Fig. 4 (left panel:  $k$ -space; right panel: Fourier transforms,  $k^2$ -weighted). From the Fourier-transformed spectra it is clear that at least two shells contribute to the oscillations observed in the initial complex—the second one being reflected by a pronounced shoulder of the first scattering peak. After reduction, a new neighbor appears at ca.  $2.5\text{ Å}$  (uncorrected), most likely palladium. These observations are confirmed by the results of the numerical analysis given in Table 2. In this analysis, nitrogen and oxygen neighbors cannot be differentiated, and other light atoms (Cl) cannot be safely excluded. In the as-prepared

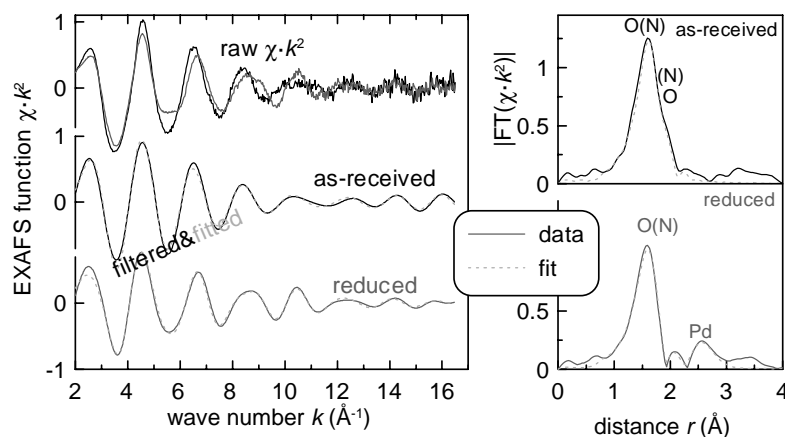


Fig. 4. EXAFS spectra for palladium adsorption complex with chitosan, as-received and reduced forms; for numerical parameters of models (see Table 2).

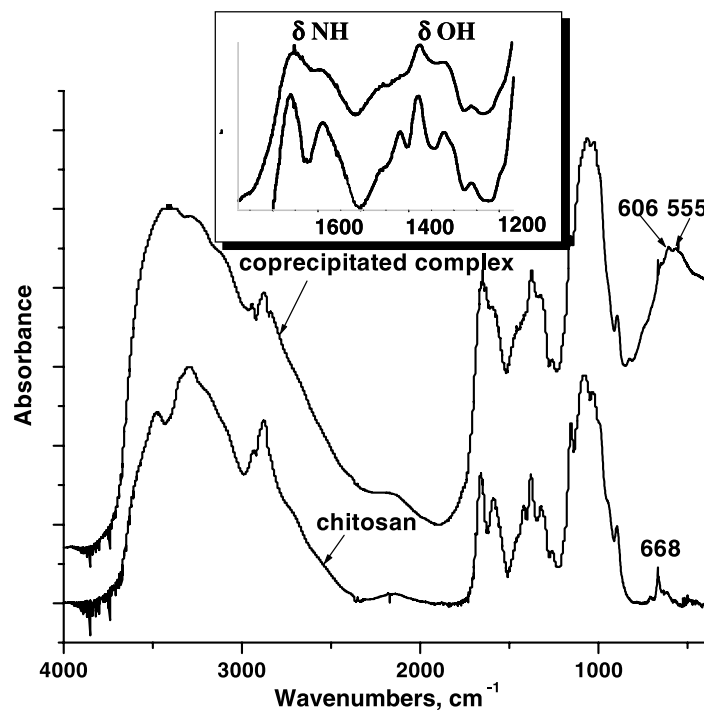


Fig. 5. IR spectra of initial chitosan and coprecipitated chitosan palladium complex.

complex, the central Pd ion is coordinated by four light atoms, two each at equal distances. In the reduced form, the Pd–Pd coordination has a distance near that known from bulk palladium ( $2.78 \text{ \AA}$  as compared with  $2.742 \text{ \AA}$ ), but a very low coordination number of 1 while there are now three light neighbors at the shorter of the two distances found in the initial sample ( $2.03 \text{ \AA}$ ).

### 3.2. Coprecipitation complex

#### 3.2.1. IR spectroscopy

With the coprecipitation complex, the band in the low-frequency range assigned to the Pd–ligand interaction appears at a higher frequency than with the adsorption com-

plex (Fig. 5): it is characterized by a maximum at  $606 \text{ cm}^{-1}$ , but the structure of the band is more complex, exhibiting shoulders and a second maximum at  $555 \text{ cm}^{-1}$ . Along with the intensity changes in the region of NH-group deformational vibrations already seen with the adsorption complex ( $1680\text{--}1500 \text{ cm}^{-1}$ ), there are now also significant changes in the intensity distribution between bands in the region of OH group bending vibrations between  $1400$  and  $1300 \text{ cm}^{-1}$ .

#### 3.2.2. EXAFS

The EXAFS spectra of the initial and the  $\text{NaBH}_4$ -reduced coprecipitation complex are shown in Fig. 6 (left panel:  $k$ -space; right panel: Fourier transforms,  $k^2$ -weighted). They differ significantly from those measured with the adsorption

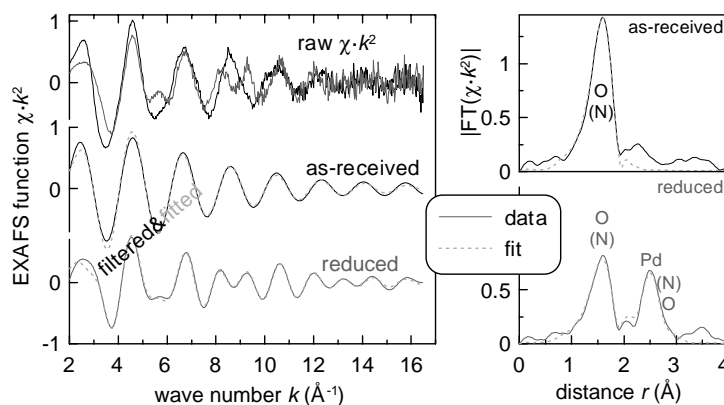


Fig. 6. EXAFS spectra for palladium coprecipitation complex with chitosan, as-received and reduced forms; for numerical parameters of models (see Table 3).



Table 3  
EXAFS results for the coprecipitation complex between palladium and chitosan: model parameters

Sample	Bond	R (Å)	CN	$\sigma^2$ ( $\times 10^{-3} \text{Å}^2$ )	$\Delta E$ (eV)
As-prepared	Pd–O <sup>a</sup>	2.030 (7)	3.9 (8)	4 (1)	13 (1)
Reduced	Pd–O <sup>a</sup>	2.024 (8)	2.3 (4)	5 (1)	15 (1)
	Pd–Pd	2.728 (9)	1.8 (2)	6 (1)	9 (1)
	Pd–O <sup>a</sup>	3.38 (4)	3 (1)	19 (15)	15 (1)

Values shown in parentheses are the standard errors.

<sup>a</sup> Light element, O or N.

complex (Fig. 4). The spectrum of the initial coprecipitation complex is an attenuated harmonic oscillation which indicates that there is only one contributing shell. This can be clearly seen in the Fourier-transformed spectrum (Fig. 6, right upper panel). After reduction, the oscillations are more complex than with the reduced adsorption complex, obviously due to a stronger Pd–Pd contribution. The Fourier transform (Fig. 6, right lower panel) shows that there is an additional neighbor at a distance longer than that of Pd, which causes the pronounced asymmetry of the scattering feature at ca. 2.5 Å (uncorrected). These contributions are confirmed in the numerical analysis (see Table 3). It yielded four light neighbors at equal distances for the initial complex, and an entirely different Pd coordination for the reduced sample. Along with two light neighbors, there are now two Pd atoms at a distance near to that in bulk Pd (2.728 Å as compared with 2.742 Å) and three more light neighbors at 3.4 Å.

## 4. Discussion

### 4.1. Adsorption complex

In the IR spectrum of the Pd–chitosan complex obtained by the adsorption of aqueous PdCl<sub>2</sub>, an intense band appears at 474 cm<sup>-1</sup>, which is absent in the pure chitosan (Fig. 1). This is in good agreement with IR-spectroscopic data for the complex [Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]: there, the stretching vibrations of the Pd–N bonds were found at 476 cm<sup>-1</sup> [22]. Since the polymeric chitosan can coordinate the metal via amino groups or via hydroxyl groups, this band can be ascribed to stretching vibrations of Pd–N or Pd–O bonds [23]. The lack of changes in the intensity distribution of the OH-deformation vibrations (1400–1300 cm<sup>-1</sup>) indicates that the coordination is predominantly via amino groups. Summarizing the IR data, we can assume that preparation by adsorption leads to a complex similar to [Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], where the Pd metal is surrounded by two (monodentate) R–NH<sub>2</sub> and two additional ligands.

The XPS spectrum of the initial adsorption complex of palladium with chitosan exhibits a single signal that corresponds to bivalent palladium ( $E_b$  (Pd 3d<sub>5/2</sub>) = 337.8 eV) (Fig. 3). This indicates that the valence state of palladium

is conserved during the immobilization on the chitosan surface, i.e. a Pd(II) surface complex is formed. The binding energy of the adsorption complex is rather high as compared with values known for Pd(II)–O compounds (ca. 337.2 eV). Reasons for this difference could be the rather small coordination number of palladium in the complex or the presence of additional chlorine ligands (chlorine was detected by XPS and elemental analysis).

The EXAFS spectra gave more detailed insight into the structure of the adsorption complex. Two light neighbors were found at a distance of 2.04 Å from the central Pd atom (Fig. 4 and Table 2), and oxygen and nitrogen are the most likely candidates for their chemical identity. Unfortunately, these elements cannot be distinguished by their scattering properties, and their radii are too similar to allow a differentiation as well. The value of 2.04 Å may well be an average of slightly differing distances for Pd–N and Pd–O, but on the basis of the IR spectrum discussed above, Pd–N coordinations are more likely. In addition, a second light neighbor could be identified at 2.18 Å, with a coordination number of 2. This is an unexpected high length for a Pd–O bond, but the history of the samples allows other explanations. Thus, the somewhat larger distance could be an indication for the presence of chlorine, which would result from imperfect hydrolysis of the Pd–Cl bonds in the parent PdCl<sub>2</sub> reagent. Indeed, the presence of chlorine in the sample prepared by adsorption from the aqueous PdCl<sub>2</sub> solution was detected by elemental analysis, by contrast to the coprecipitation

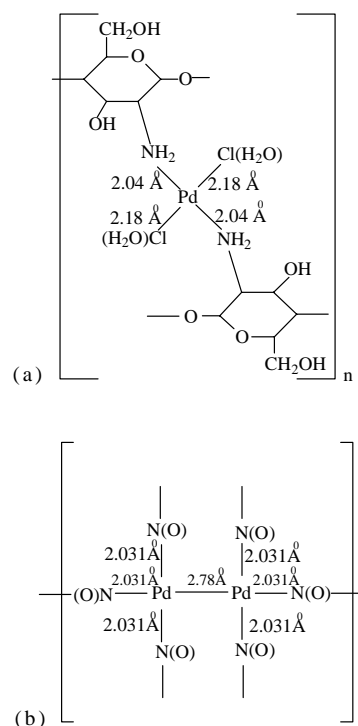


Fig. 7. (a) Pd–chitosan complex formed by adsorption from an aqueous PdCl<sub>2</sub> solution: proposed structure and (b) coordination sphere of Pd(0) atoms in the reduced adsorption complex: proposed structure.

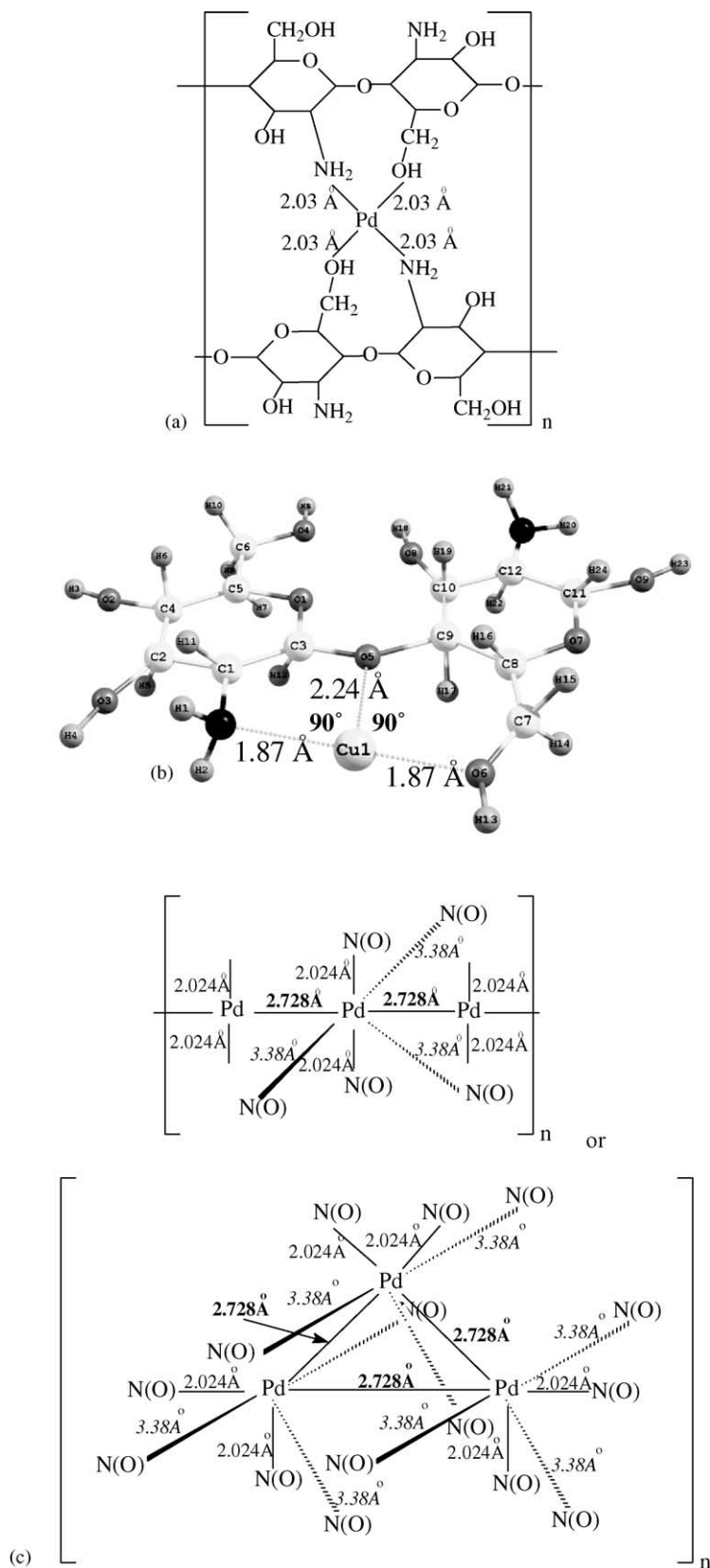


Fig. 8. (a) Pd-chitosan structure formed by coprecipitation of chitosan with a homogeneous Pd-chitosan complex: proposed coordination sphere; (b) bivalent metal cation coordinated with chitosan: molecular structure derived from DFT calculations [16]; and (c) coordination sphere of Pd(0) atoms in the reduced coprecipitation complex: proposed structures.



sample. An alternative explanation for the neighbor at 2.18 Å would be the presence of H<sub>2</sub>O molecules as ligands in the palladium sphere. Thus, in accordance with EXAFS, IR and XPS data the structure shown in Fig. 7a is proposed for the adsorption complex.

After reduction of the adsorption complex, the XPS spectrum exhibits a signal that corresponds to Pd(0) ( $E_b$  (Pd 3d<sub>5/2</sub>) = 335.7 eV) in addition to the signal of Pd(II) ( $E_b$  (Pd 3d<sub>5/2</sub>) = 337.8 eV). In the EXAFS spectrum, the light neighbor at 2.18 Å disappeared, which may indicate the removal of chlorine during the reduction (Fig. 4). Moreover, after the reduction, a palladium neighbor with a bond length typical of metallic Pd (2.78 Å) appeared, but with the very low coordination number of 1. This may indicate the formation of a dimer structure as proposed in Fig. 7b.

After reoxidation of the reduced adsorption complex with hydrogen peroxide, the XPS signal of bivalent palladium was reproduced, however, the binding energy was shifted toward lower energies ( $E_b$  (Pd 3d<sub>5/2</sub>) = 337.0 eV). This result indicates changes in the ligand environment of palladium: the appearance of additional ligands, a possible partial change in Pd(II) coordination. The active site of an oxidation catalyst should be able to undergo reversible redox transformations. The result obtained here is not quite unambiguous in this respect. It could be demonstrated that the Pd ion readily changes its oxidation state from Pd(II) to Pd(0) and vice versa, but in the procedure chosen, the Pd coordination sphere was obviously affected. The catalytic properties of these samples will be reported in a following publication.

#### 4.2. Coprecipitation complex

As mentioned above, the band assigned to Pd–N and Pd–O stretching vibrations appears at higher frequencies in the coprecipitation complex (606 cm<sup>-1</sup>), and its structure is more complex than in the case of the adsorption complex (Figs. 2 and 5). These facts indicate the formation of stronger Pd–N bonds in the complex prepared by coprecipitation. The stronger binding is probably related to complexing with chelate ligands instead of monodentate ligands. In the case of coprecipitation, where residual halogen atoms are removed by the alkali treatment during preparation, the ligand environment of palladium may consist only of ligands provided by the polymeric matrix. The structure will be most stable if these ligands are chelating or bidentate. Such structure would include the functional groups of two neighboring chitosan rings. These ligands will coordinate to the central palladium either via the nitrogen atoms of the amino groups or via the oxygen atoms of the hydroxyl groups. Due to the spatial structure of chitosan in which each ring is at a certain angle relative to the adjacent rings [24,25], the intermediate variant is the most plausible, where one chitosan ring provides a nitrogen atom and the other one an oxygen atom. The intensity changes of IR bands in the region of OH bending vibrations in chitosan (1400–1300 cm<sup>-1</sup>) found

with the coprecipitated complex is an additional evidence for the metal coordination by chitosan hydroxyl groups.

From the EXAFS spectrum measured for the coprecipitation sample it could be concluded that ca. four light neighbors are present in the coordination sphere of palladium at distances of 2.030 Å (Fig. 6 and Table 3). As mentioned above, EXAFS does not allow to differentiate between N and O at these positions. Only one distance has been identified. Although this may be the result of some averaging, any difference between Pd–N and Pd–O distances should be below 0.1 Å, else they would have been differentiated. Taking into account the IR data for the coprecipitated complex, we propose the structure shown in Fig. 8a for the coprecipitation complex where bivalent palladium is in a square-planar chelated coordination. This structure resembles molecular structures derived for complexes of divalent cations with chitosan from density functional calculations, which were published recently (Fig. 8b [7]). Remarkably, the DFT calculations also resulted in identical Pd–N and Pd–O distances, which supports the idea that they are close to the structures formed in our preparation.

From the EXAFS spectrum of the reduced coprecipitated complex, a Pd–Pd metallic coordination with a coordination number of 2 was derived while three more light (O or N) neighbors occur at higher distances (3.38 Å, see Table 3). The former can be realized in a triangular structure or in a (long) open chain of Pd atoms (Fig. 8c). The presence of three light atoms in the second coordination sphere at a distance of 3.38 Å suggests that bulk metal particles are not formed. It should be noted that the Pd–Pd distance in the reduced coprecipitation complex (2.728 Å) is shorter than that in the (linear) adsorption complex (2.78 Å) and even in a palladium foil (2.742 Å). We therefore prefer the triangular structure over the open chain because the former is more compact and the Pd–Pd bond is not linear.

##### 4.2.1. Preliminary catalytic tests

The complexes prepared were preliminary tested in oxidation of terminal olefins with oxygen. It was found that in neutral media, the coprecipitative complex causes olefin isomerization and shows virtually no activity in the formation of oxidation products. In the case of the adsorption-type complexes the main process is the olefin oxidation. As a reoxidizing agent, we used classical Wacker systems, such as hydrogen peroxide in acidic media and CuCl<sub>2</sub> with oxygen. Thus, the data obtained show that heterogenized palladium chitosan complexes are capable of catalyzing the olefin oxidation [26]. Detailed catalytic investigations are in progress now.

## 5. Conclusions

1. On the basis of IR and EXAFS investigations, it can be concluded that the structure of palladium complexes with chitosan depends on the preparation procedure. Upon

adsorption of Pd(II) from an aqueous PdCl<sub>2</sub> solution, a coordination sphere near to that in a [Pd(NH<sub>2</sub>R)<sub>2</sub>Cl<sub>2</sub>] complex was formed, whereas a chelate complex with palladium coordinated to amino and hydroxy groups of chitosan rings was formed when a homogeneous Pd–chitosan complex was precipitated by increase of the pH value.

2. XPS and EXAFS results infer that the complexes undergo different structural changes upon reduction with NaBH<sub>4</sub>. The aggregation of Pd remains very low, but the structure formed from the chelate complex obtained by coprecipitation has a higher degree of aggregation (possibly Pd<sub>3</sub> triangular structures as opposed to Pd<sub>2</sub> dimers in the case of the adsorption complex).
3. The possibility of reversible redox transformations of palladium immobilized on a chitosan matrix was studied by XPS. It was shown that the redox state can be easily switched between Pd(II) and Pd(0), however with concomitant changes in Pd coordination sphere as evident by changes of the Pd<sup>2+</sup> 3d<sub>5/2</sub> binding energy. It will be shown in a future paper that these materials exhibit interesting catalytic properties in oxidation reactions.

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