Reactions of Immobilized Palladium (II) Complexes with Carbon Monoxide

Alexander Fedorovich Novikov

Saint Petersburg National Research University of Information Technologies, Mechanics and Optics (ITMO University), Saint Petersburg, Russia

Email address:
alexfednov@gmail.com

Abstract: Palladium (II) complex compounds were immobilized on the dried inner surface of nanoporous silicate glass. The solid specimens containing the Pd(II) salts and organic complexes were fabricated and tested in respect to their spectral reaction on carbon monoxide in atmosphere. The specimens have demonstrated reversible color changes while interacting with carbon monoxide. The reaction mechanisms are supposed to be connected with formation and dissociation of the coordination compounds on the pore surface. Chemical interpretation of the processes is given.

Keywords: Palladium (II) Complex Compounds, Carbon Monoxide, Spectrochemistry of Surface Complexes

1. Introduction

It is common knowledge that the carbon monoxide (*CO)* is able to reduce the Palladium ion Pd^{2+} in solution to metallic Palladium [1]:

$$PdCl_2 + H_2O + CO \rightarrow Pd \downarrow + CO_2 \uparrow + \\ + 2HCl, or :$$

$$[PdCl_4]^{2-} + H_2O + CO \rightarrow Pd \downarrow + CO_2 \uparrow + \\ + 2H^+ + 4Cl^-.$$
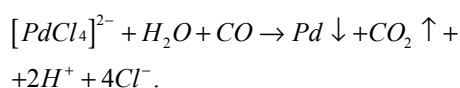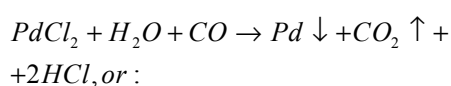
The latter reaction proceeds supposedly in two steps as follows [2]:

$$[PdCl_4]^{2-} \xrightarrow{+CO} [PdCOCl_3]^- \xrightarrow{+H_2O} \\ \rightarrow Pd \downarrow + CO_2 \uparrow + 2H^+ + 4Cl^-.$$
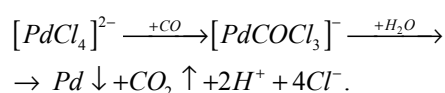
The reaction proceeds in irreversible way and a salt solution instantly gets colorless. However, the time spread process may be provided with use of the more complicated solution composition and procedure as reported in [3].

In order to understand the process more comprehensively, it makes sense to study it not in liquid solution but directly without any solvent influence. This seemed to be available with use of the certain Palladium (II) complexes being immobilized on the properly pretreated dielectric surface. As the appropriate substrates in similar applications proved to be the matrices made of nano-scale porous silicate glass. Presently, the structure and properties of nanoporous glasses as they are have been thoroughly studied by many researchers [4-6].

Methods for precipitation of various dopants within nano-scale porous silicate glass have been invented enough long time ago [7]. However, only during recent decades the intensive studies have been carried out having as an object the organic and inorganic molecular clusters down to the single molecules being immobilized on a highly developed surface of the nanoporous glass [4, 5, 8, 9].

Among others the spectral methods have proved its applicability and effectiveness in molecular physics and chemistry. In principal, these methods allow to detect optical signals produced even by single molecules [10].

In the meanwhile the nanoporous glass also is not anyhow a passive substrate for the adsorbed substances, but on the contrary, the inherent matrix properties exert a critical impact on the composition properties on the whole. In contrast to the molecules being dissolved in the liquid solution, the same molecules being immobilized within nanoporous matrix behave substantially in different way. This situation causes

certain peculiarities in the spectral characteristics of immobilized molecules that are not event in case of the molecules in solutions. This matter is of special interest as concerns a chemism of the molecular interaction. Investigations of these processes might open good application prospects of the obtained results.

As a complexing agent, namely a Pd^{2+} ion was selected with taking into consideration the following ideas. This ion is able to form the number of intermediate carbonyl-halogenide coordination compounds and therefore to produce a gradual color transition of the composition samples. The Pd^{2+} ion has an electronic configuration d^8, thus it might form the donor-acceptor bound with CO electron pairs.

2. Subjects and Methods

2.1. Sample Preparation

Nanoporous samples were fabricated using the stepwise thermal and chemical treatment following the well-known Vycor process [4, 5]. Original solid glass was liquated sodium-borate-silicate glass (sodium oxide – 6.8 mass. %, boron oxide – 26.7%, silicon oxide – 66.0%, the rest – other components) containing the separated phases. After having been treated in an aqueous solution of hydrochloric acid HCl (3N), a sodium-borate phase was leached out, thereafter the samples were annealed in air at +550°C. Such procedures resulted in a through-out open porous structure within a substantially silica framework.

Next a procedure followed of the nanoporous matrix impregnation in solution of the selected Palladium salt. The procedure lasted until sorption equilibrium having been achieved. The salt molecules were forced to penetrate into nanoporous glass from the acetone, ethanol, or dimethyl sulfoxide solutions. The samples were then extracted from the initial solutions and dried in air at +50°C in purpose to evaporate the solvent out of the matrix pores.

By means of the treatment described the salt molecules were fixed onto pores surface.

The specimens under test were the plates of various thicknesses within 0.2 – 1.0 mm.

2.2. Spectral Measurements

The absorption spectra of the porous glassy samples containing the Palladium compounds and impregnating solutions were run on the spectrophotometers U-3200 (Hitachi, Japan), Lambda 19 (Perkin-Elmer, USA) and СФ-26 (LOMO, Russia) within wave range of 300 – 800 nm.

During measurements, the samples were put into optically transparent cell being blown-through with CO containing air. Before taking readings, the specimens were kept in the analyzed gas mixture for sufficient time (10 min or longer). The reference spectral characteristics related to the specimens having been previously kept in normal laboratory atmosphere (relative humidity of 50% at 20°C).

3. Results and Discussion

3.1. Studies of Original Nanoporous Matrix

Small-angle X-ray techniques as well as a routine processing the adsorption isotherms in the area of capillary condensation have revealed the pore size distribution with maximum in vicinity of 8 – 9 nm [9], the porosity being 28% of the total sample volume. Specific area, calculated from a specific bending point on the isotherm curve, turned out to be about 105 m^2/cm^3.

The studied porous glass exhibits an absorption isotherm of A-V type (A-subtype) according to the Gregg's classification [11]. This fact witnesses the long-capillary pore configuration. The resulted porous structure was permeable for gases and liquids, and the samples were practically transparent in the visible wave range.

3.2. Spectral Studies of Immobilized Palladium (II) Chloride

In Fig. 1 (curve 1) an absorption spectrum of the impregnating solution is presented. This solution is the acidulous water solution of $PdCl_2$. The spectrum shape is typical for the planar tetra-coordinated complexes of the Platinum row metals. Specifically, an absorption band at 350 nm may be assigned to the transition connected with a charge transfer from ligand to metal in the dimer molecular ions $[Pd_2Cl_6]^{2-}$ [12, 13]. A broader band at 456 nm most probably belongs to the d-d transitions within Palladium ions. The curve 2 in Fig. 1 presents the spectrum of nanoporous sample containing the immobilized Palladium (II) chloride complexes. Lowering of the adsorption maxima may be caused by the restriction of the vibrational freedom degree of particles immobilized on the pores surface.
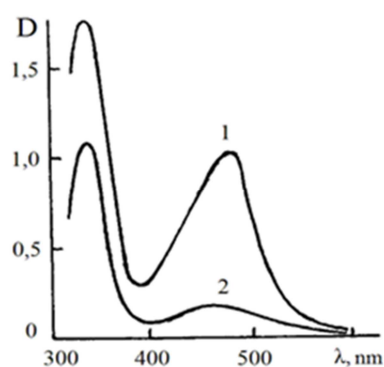

Fig. 1. *Absorption spectra of PdCl₂. 1– acidulous water solution of PdCl₂; 2– nanoporous sample processed in this solution.*

In Fig. 2, a spectral response of the nanoporous sample on the carbon monoxide in atmosphere is presented. As one can see, the response was significant but rather slowed down one. Air blowing the optical cell with clean air returned the spectrum to the initial shape, however, the sample spectrum recovered not entirely. Nevertheless the very fact of spectral recovery witnesses that metallic palladium reduction does not take place in this case. Most probably the intermediate

complexes of the Palladium carbonyl-halogenides are formed on the dry pores surface. The most stable among them are the monomeric complexes *[PdCOCl₃]⁻*, or the dimer ones *[Pd₂(CO)₂Cl₆]²⁻*. In general, the process may be written in such a way:

$$[PdCl_4]^{2-}_{surf.} \xrightarrow{+CO} [Pd(CO)Cl_4]^{2-}_{-Cl^-} \rightarrow \rightarrow [Pd(CO)Cl_3]^{-}_{-Cl^-} \rightarrow [Pd(CO)Cl_2].$$
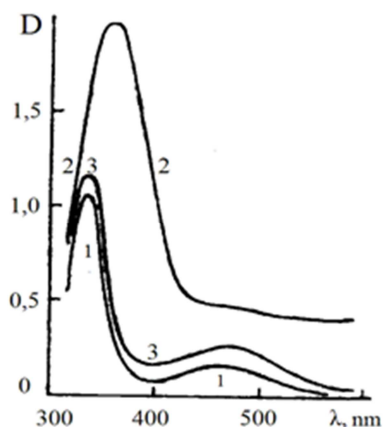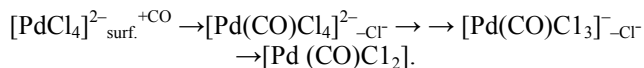

Fig. 2. Absorption spectra of the processed nanoporous sample: 1– in the initial atmosphere; 2 – in the CO atmosphere; 3– in the initial atmosphere again.

In essence, this reaction may proceed following to an associative mechanism of the S_N2_{lim} type with formation of the rectangular pyramid. For avoiding the irreversible signal component, the glass surface should be chlorinated, however, it helped rather weakly.

In addition, the *CO* molecules could also take a bridge position between the adsorbed monomeric complexes. Some of them could remain fixed in this position on the pore surface and provide an observed irreversible component of the spectral response. If so, cycling the *CO* attacks on the sample might improve the situation.

3.3. Spectral Studies of Immobilized Palladium (II) Organic Complexes

The enough encouraging results have been obtained with using the more complicated compound such as *Pd₂*-di-μ-dibromo-bis-(di-*n*-propylsulfoxide):
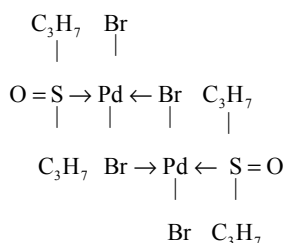
Noteworthy is the complex being initially a bridged dimer [14].

As an optimum solvent, the dimethyl sulfoxide compound was selected because of its being homologous to dipropyl sulfoxide. Spectrum of this solution is displayed in Fig. 3

(curve 1). Compared with Palladium (II) chloride, a spectrum in Fig. 3 demonstrated the same two bands revealing presence of the dimeric molecules and electron transitions within Pd^{2+} ions. However, the latter band is less expressed and shifted to the shorter wave lengths.
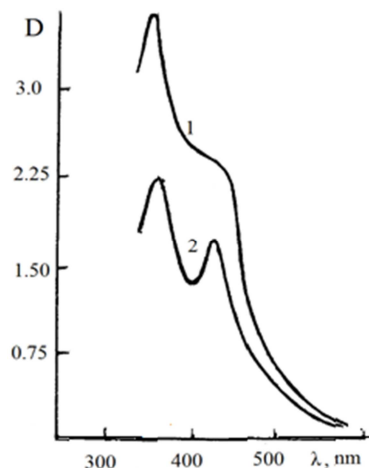

Fig. 3. Absorption spectra of the dimethyl sulfoxide solutions of the Pd(II) complex: 1 – before barbotage; 2 – after barbotage.

These dimeric complexes dissociate to the monomeric ones in presence of the carbon monoxide molecules (see the reaction below) [15]. In Fig. 3 (curve 2) a spectrum of the bubbled solution is presented, one can see the lowering of the dimer absorption band. Indeed, after barbotage procedure the solution gets clearer, and the precipitation process takes place. Surely, the sediment was thoroughly filtered off.
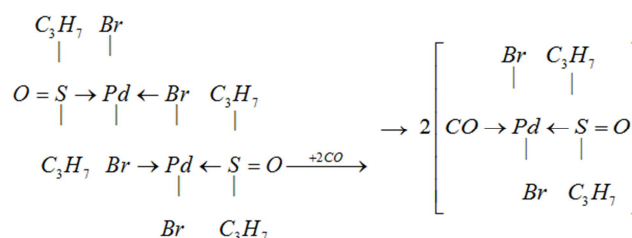
Taking into consideration such behavior of the system, we have used a procedure of the porous samples impregnation in solutions of both non-bubbled and previously bubbled by the gaseous carbon monoxide. In Fig. 4 the corresponding spectra are presented.

The spectral response under the same conditions was almost entirely reversible. The irreversible reduction of the Pd^{2+} ion by the *CO* molecules does not take place here. The reaction mechanism includes only a bridging process accompanied by configuration changes in a coordinative sphere of the immobilized ion. Therefore an optical response is exceptionally due to the *CO* molecules, and it provides very high selectivity of the sensor signal.

So, it has been demonstrated that one of the transition metal ions Pd^{2+}, being immobilized on the nanopores surface, may form enough stable complexes with certain gas molecules such as carbon monoxide *CO* accompanied by the specific color changes.
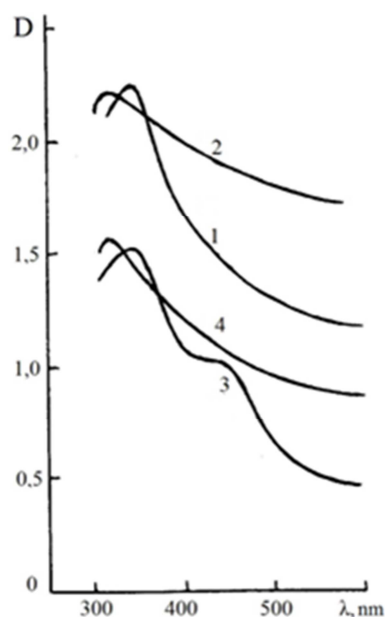
Fig. 4. Absorption spectra of the nano-porous samples processed in the dimethyl sulfoxide solutions of the Pd(II) complex: 1 – sample from the non-bubbled initial solution; 2 – the same in the CO atmo-sphere (70% vol.); 3 and 4 – the same from the bubbled solutions, respectively.

For systematisation and interpretation of these phenomena, a Lewis' and Pearson's conception about Hard and Soft Acids and Bases (HSAB) [16, 17] might be applied. According to the HSAB conception, all the Lewis' acids and bases (electrophilic and nucleophilic agents, respectively) may be characterised upon its ability to form the stable acid – basic complexes in course of the electrophilic (nucleophilic) substitution reactions. A characteristic parameter is here a rate of the complex formation.

Due to the numerous studies it has been found that the ions such as H^+ and Si^{4+} etc. and some oxides including SiO_2 play a role of the hard acids. The ions Pd^{2+}, Ag^+ as well as neutral metal atoms may be assigned to the soft acids. On the other hand, the soft bases are the molecules CO, dimethyl sulfoxide $(CH_3)_2SO$, and others.

R. Pearson had formulated and substantiated a following laconic principle: "Hard acids preferably do compounds with hard bases and soft acids with soft bases, otherwise the stable compounds and strong bonding do not formed" [16].

The Lewis – Pearson's conception is very useful and productive in many cases. However, it has till now rather qualitative character and needs further proves. Our experimental results most likely present one of such proves. Indeed, the Pd^{2+} ions (soft acid) does not form the stable compound with superficial silica groups (SiO_2 is a hard acid). So, the immobilized Pd^{2+} ions maintain its reactivity with soft bases such as CO, $(CH_3)_2SO$ and with more complicated homologous ligands. The more so as the corresponding color change rate is rather low – about five min).

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