Anais da Academia Brasileira de Ciências (2008) 80(2): 263-269
(Annals of the Brazilian Academy of Sciences)
ISSN 0001-3765
www.scielo.br/aabc

Thermal properties of metal-metal bonded Pd(I) complexes supported onto porous Vycor glass

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Manuscript received on October 6, 2006; accepted for publication on October 23, 2007;
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ABSTRACT

Thermal behavior of the complexes $Pd_2(dppm)_2Cl_2$, $Pd_2(dppm)_2(SnCl_3)Cl$ and $Pd_2(dppm)_2(SnCl_3)_2$ (dppm = bis[diphenylphosphino(methane)], $((C_6H_5)_2PCH_2P(C_6H_5)_2)$ in the solid state and immobilized onto porous Vycor glass was studied. Similar decomposition mechanisms were observed for the solid and immobilized complexes, with a small thermal stabilization upon immobilization. The decomposition products were characterized by X-ray diffractometry, Raman and diffuse reflectance infrared spectroscopy, which indicated the presence of a mixture of metallic palladium and oxidized species such as PdO, condensed phosphates, SnO_2 and SnP_2O_7. According to X-ray diffractometry, the decomposition products of the immobilized complexes presented higher amounts of PdO than the solid-state residues, probably as an effect of interactions with silanol groups present in the glass surface.

Key words: palladium(I) complex, porous Vycor glass, bis[diphenylphosphino(methane)], thermogravimetric analysis.

INTRODUCTION

The study of supported organometallics and transition metal complexes is motivated mainly by applications as catalysts (Ando et al. 2004, Kureshi et al. 2004) and molecular precursors to advanced materials such as gas sensors (Alves et al. 2005, Silva et al. 2006), semiconductors, and metallic particles (Sunil et al. 1993). In particular, heterogeneous catalysts containing Pd or Pt have been studied owing to their activity in oxidation of CO, hydrogenation, (Evrard et al. 2004) and electrochemical oxidations (Yang and McElwee-White 2004). A previous paper by Richmond and co-workers reported the preparation of dinuclear phosphine-bridged palladium(I) species and their silica-bound analogues as catalysts for the cyclization of aminoalkynes, showing that in some cases the catalytic activity is improved by the higher thermal stability of the supported catalyst (Richmond et al. 2002).

The family of complexes of interest here includes the complex containing metal-metal bonded Pt(I) atoms $Pt_2(dppm)_2Cl_2$ (Glocking and Pollock 1972) and its palladium analogue, which can be used as homogeneous catalysts in several reactions (Kirss and Eisenberg 1989). The derivatives of $SnCl_2$ insertion into Pd-Cl bonds of $Pd_2(dppm)_2Cl_2$ also catalyze the alkoxycarbonylation of terminal alkenes (Nguyen et al. 2005). In this context, the thermal behavior of free and supported complexes is important both to evaluate the thermal stability and to identify decomposition products. However, for the complexes of interest here this aspect was still unexplored.

The interest in the reactivity of single bonded Pd_2 moieties for sensor phases is a growing area and previous attempts to immobilize similar com-

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pounds onto polystyrene for application in separation of gases were unsuccessful due to steric demands (Lee et al. 1986). Recently we described the immobilization of $Pd_2(dppm)_2Cl_2$, $Pd_2(dppm)_2(SnCl_3)Cl$, and $Pd_2(dppm)_2(SnCl_3)_2$ onto porous Vycor glass (Gimenez and Alves 2002, 2004), which proved to be suitable precursors for gas sensing systems (Alves et al. 2005, Silva et al. 2006). We were further interested in studying the thermal stability of these immobilized species, since the gas insertions into the metal-metal bond can be reverted both by heating and inert-gas flow. In this paper we report the thermogravimetric study of the complexes $Pd_2(dppm)_2Cl_2$, $Pd_2(dppm)_2(SnCl_3)Cl$, and $Pd_2(dppm)_2(SnCl_3)_2$, both in the solid state and immobilized onto porous Vycor glass, as well as the characterization of the decomposition products by XRD, DRIFT, and Raman spectroscopy.

MATERIALS AND METHODS

PREPARATION OF SOLID AND SUPPORTED COMPLEXES

All the syntheses were carried out using solvents purified and dried by standard methods. $PdCl_2$, dppm and anhydrous $SnCl_2$ were purchased from Aldrich and used without further purification. The complexes $Pd_2(dppm)_2Cl_2$ (**1**), $Pd_2(dppm)_2(SnCl_3)Cl$ (**2**) and $Pd_2(dppm)_2(SnCl_3)_2$ (**3**) were prepared by methods described in the literature (Balch and Benner 1982, Olmstead et al. 1979).

IMMOBILIZATION EXPERIMENTS

The complexes were immobilized onto 1-mm thick polished Vycor 7930 glass plates. Immobilization experiments were carried out by immersion of 10 × 10 × 1 mm glass plates into 1 10^{-3} mol L^{-1} methylene chloride solutions of the complex at room temperature for 24 hours. The solvent was removed under vacuum. The PVG-supported complexes will be referred in the text as

$$PVG/\mathbf{1}(PVG/Pd_2(dppm)_2Cl_2),$$
$$PVG/\mathbf{2}(PVG/Pd_2(dppm)_2(SnCl_3)Cl) \quad \text{and}$$
$$PVG/\mathbf{3}(PVG/Pd_2(dppm)_2(SnCl_3)_2.$$

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analyses were carried out in a TA Instruments 2960, using platinum sample holders, under the dynamic flow of dry synthetic air (20 mL min^{-1}), at a heating rate of 10 K min^{-1}.

PYROLYSIS EXPERIMENTS

All pyrolysis experiments of solid and immobilized complexes were carried out in platinum crucibles under air for 24 h at specified temperatures.

X-RAY DIFFRACTOMETY (XRD)

X-ray diffractograms were obtained with a Karl Zeiss URD-6, using Cu-$\kappa\alpha$ radiation ($\lambda = 1.54060$Å), with a step 2θ 0.02/0.4 s.

RAMAN SPECTROSCOPY

Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 3000, coupled to an optical microscope with resolution 1.5μm and a He-Ne ($\lambda = 632.8$ nm) laser source. Sampling was accomplished by scanning different surface regions of the sample placed onto glass sheets.

FOURIER TRANSFORMED DIFFUSE REFLECTANCE INFRARED ANALYSIS (DRIFT)

Diffuse reflectance infrared spectra were obtained with a Nicolet 520 spectrophotometer in the spectral range 4000-400 cm^{-1} using KBr as reference.

RESULTS AND DISCUSSION

Figure 1 shows the TG curves for the solid samples, while their corresponding data are displayed in Table I. The decomposition of **1** starts at 471 K with an abrupt mass loss up to 837 K corresponding to a 62% loss (calculated 62%), attributed to elimination of one $P(Ph)_2CH_2Cl_2$ active radical and one dppm molecule. Formation of similar radical species was reported by Zayed and co-workers in the thermal decomposition of mononuclear $Pt(dppm)Cl_2$ complexes in the range 393-773 K (Zayed et al. 1999). In the present case a further decomposition step can be observed above 837 K, with a mass loss of 13% attributed to the elimination of residual phosphine species and reduction of PdO eventually formed on the surface. The formation of metallic Pd residues or Pd/PdO mixtures rely on the pyrolysis conditions as well as on the presence of groups in the molecular structure able to generate reducing conditions during decomposition.

In the TG curve of compound **2**, the mass gain starting from 474 K may be attributed to oxygen uptake. The mass increase at relatively low temperatures by oxygen absorption is commonly observed for Pd and Pt complexes such as [Pd(PPh$_3$)$_4$] and [Pt(PPh$_3$)$_4$], rendering species such as CO_3^{2-} and Ph$_3$PO (phosphinoxide) (Barbieri et al. 1995). As verified in Figure 1, the mass gain is followed by a gradual mass loss from 546 K to 968 K. No clear plateau can be defined but the curve derivative shows a broad feature from 546 to 822 K corresponding to a 49% loss. Probably the decomposition involves elimination of P(Ph)$_2$CH$_2$Cl$_2$ plus one entire dppm (expected loss: 52%).

For compound **3** the initial 2% loss due to elimination of water suggests the presence of SnCl$_2$ (hygroscopic) as an impurity. When this compound is put into CH$_2$Cl$_2$ solution the following chemical equilibrium takes place (Olmstead et al. 1979):

$$\underset{\mathbf{3}}{Pd_2(dppm)_2(SnCl_3)_2} \rightleftharpoons \underset{\mathbf{2}}{Pd_2(dppm)_2(SnCl_3)Cl} + SnCl_2$$

A large SnCl$_2$ excess is necessary in the synthesis leading to the presence of SnCl$_2$ as a product impurity. Exhaustive purification attempts by recrystallization will form compound **2** and, in fact these limitations precluded the crystal structure determination for this compound, since its earliest report (Olmstead et al. 1979). According to TG curve, compound **3** degrades with continuous mass loss from 413 K up to 916 K. In the range 586-683K the mass loss observed (24%) is coherent with loss of a P(Ph)$_2$CH$_2$Cl$_2$ radical plus a Cl$_2$ molecule (calculated 24%). The decomposition of the residue is gradative and incomplete with a final mass percent of 48%.

The decomposition products were characterized by XRD, DRIFT and Raman. According to X-ray diffraction, Figure 2, the main decomposition product of solid complex **1** is metallic palladium ($2\theta = 40.1°$, 46.6° and 68.1° (JCPDS)). For the complexes **2** and **3**, residues contain SnO$_2$ ($2\theta = 26.5°$, 34°, 38°, 51.8°) and SnP$_2$O$_7$ ($2\theta = 19.2°$, 22.3°, 37.6°) in addition to metallic palladium.

DRIFT and micro-Raman spectroscopies suggested the presence of additional phases, mostly in the case of **1**. For **1**, the Raman spectrum (Fig. 3) shows the typical features of PdO (Chan and Bell 1984), probably not detected by X-ray diffraction due to its concentration on the surface. For compounds **2** and **3**, SnO$_2$ bands near 630 cm^{-1} dominate the Raman spectra (Fig. 3). For all samples, spectra of some surface regions show a pair of broad bands at 1330 cm^{-1} and 1580 cm^{-1} indicating amorphous carbon residues (Macedo et al. 2008).

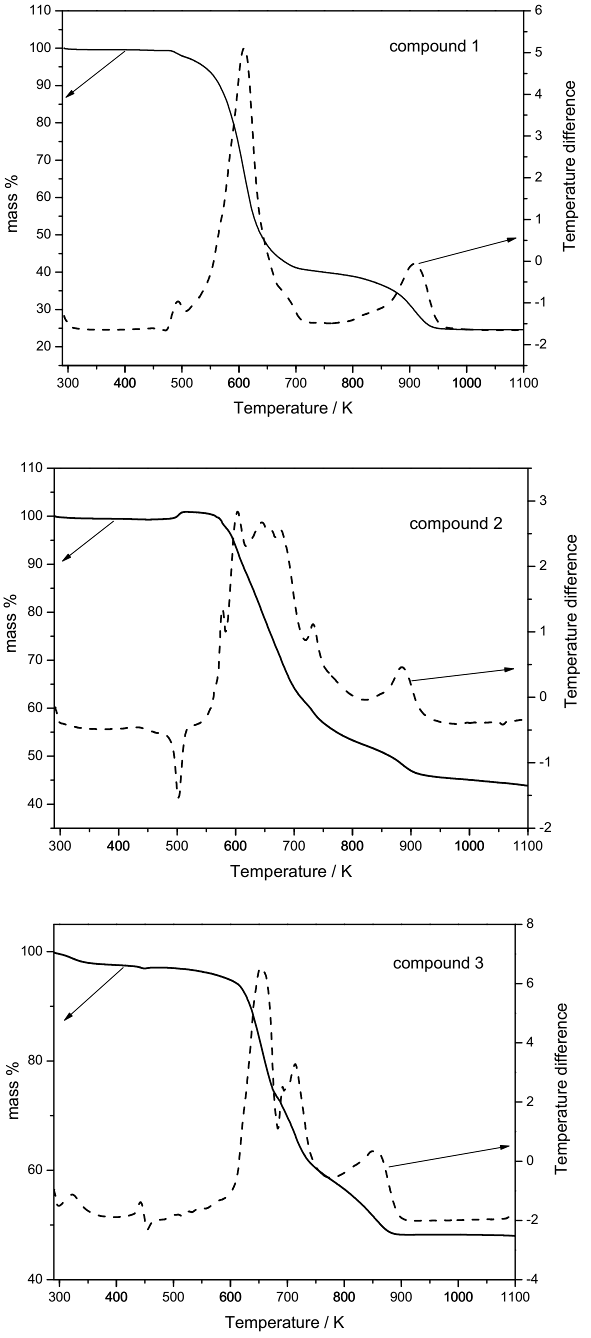

Fig. 1 – TG curves of compounds: Pd$_2$(dppm)$_2$Cl$_2$ (**1**), Pd$_2$(dppm)$_2$(SnCl$_3$)Cl (**2**) Pd$_2$(dppm)$_2$(SnCl$_3$)$_2$ (**3**).

TABLE I
Thermogravimetric data for compounds *1-3*.

Compound	T range (K)	Δ mass %	Δ mass (amu)
1	471-837	62	654 $P(Ph)_2CH_2Cl_2$ radical +dppm
	837-970	13	133
2	474-519	2 (gain)	19
	546-822	49	654 $P(Ph)_2CH_2Cl_2$ radical +dppm
	822-968	7	85
3	298-379	2	29 H_2O
	413-454	1	9
	586-683	24	341 $P(Ph)_2CH_2Cl_2$ radical + Cl_2
	683-769	14	206
	769-916	11	152

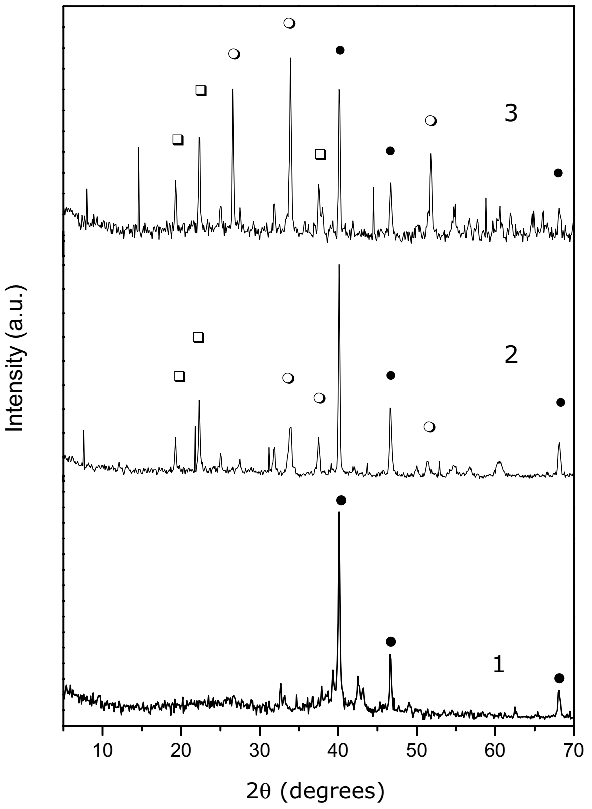

Fig. 2 – X-ray diffractograms of the decomposition products after heating compounds **1-3** at 1000°C. Assignments over the peaks refer to the phases: • = Pd, ○ = SnO_2, □ = SnP_2O_7.

DRIFT spectrum of **1** (not shown) showed a broad band around 1000 cm^{-1} suggesting the presence of condensed phosphates. For **2** and **3**, SnP_2O_7 already detected by XRD was confirmed due to the bands at 1160 cm^{-1} and 1026 cm^{-1}, assigned to ν_{sym}(P-O) and ν_{asym}(P-O) from terminal PO_3^{2-} groups, respectively, and at 748 cm^{-1} assigned to ν_{sym}(P-O) from P-O-P bridges (Hubin and Tarte 1967, Guan et al. 2005). Also a strong band at 1280 cm^{-1} can be assigned to intra-chain PO_2 moieties from condensed phosphates.

Thermal behavior of immobilized complexes was also studied. Figure 4 shows the TG curves of the PVG-supported complexes and for all samples the initial mass loss from 298 K to 423 K is due to elimination of adsorbed water from the glass surface. Up to 25% of PVG "dry mass" can be composed by adsorbed water as the pore surface is composed mainly by the very reactive silanol (Si-OH) groups (Hood and Nordberg 1938, 1942). At higher temperatures all mass losses are attributed to decomposition of the complexes and from these curves as well as from the mass loss observed for solid samples, it is possible to estimate the amount of adsorbed complexes. The related data are displayed in Table II. The thermal decomposition of PVG/**1** starts at 449 K with loss of 1%, followed by 1%. The initial decomposition temperature of the supported complex is slightly higher than in the solid state, indicating a stabi-

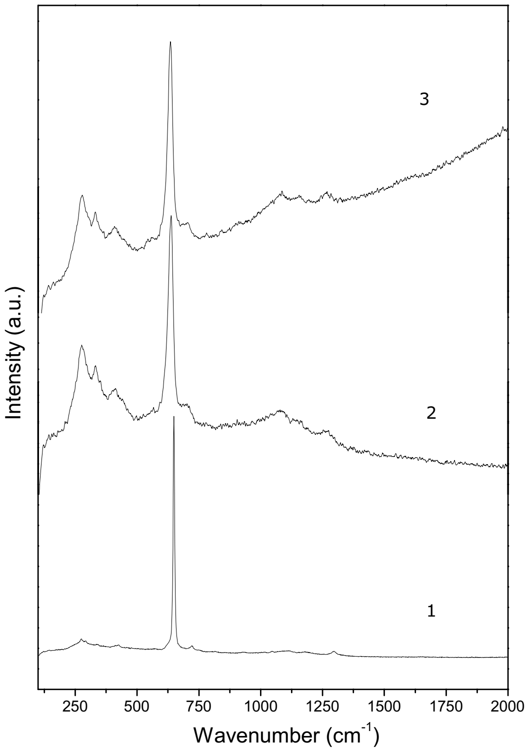

Fig. 3 – Micro-Raman spectra of the decomposition products after heating compounds **1-3** at 1000°C.

lization of the supported complex. The thermal decomposition of PVG/**2** starts at 510 K, with a deflection at 563 K and a gradual mass loss up to 919 K. Finally, for PVG/**3** mass losses at 488 K, 573 K and 740 K can be observed, slightly higher than in the solid state.

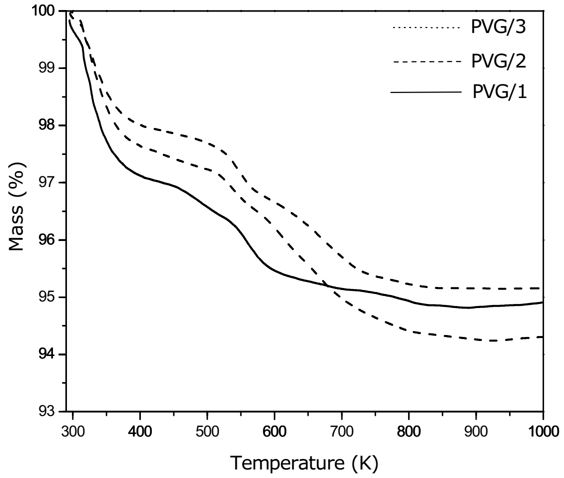

Fig. 4 – TG curves of samples: PVG/**1**, PVG/**2** and PVG/**3**.

TABLE II
Thermogravimetric data for samples PVG/*1-3*.

Sample	T range of events (K)	Δ%	%(mass) immobilized*
PVG/1	295–403	-3	3
	449–514	-1	
	533–603	-1	
PVG/2	295–395	-3	5
	510–562	-1	
	563–816	-2	
PVG/3	295–403	-2	5
	488–573	-1	
	573–740	-1	

*estimate.

As glass signals dominated the DRIFT and Raman spectra of PVG samples, only XRD was able to detect residues of the complexes. Interestingly in this case PdO peaks are observed in addition to metallic Pd for all samples, suggesting that the close contact of the complexes with silanol groups facilitates the formation of PdO, in contrast to the behavior of the solid complexes. For PVG/**2** and PVG/**3** the peaks of metallic palladium are weak in comparison to SnO_2 and SnP_2O_7 peaks.

From the results of thermal analysis and characterization of the decomposition products, we conclude that the thermal stability of the complexes is improved by immobilization onto porous Vycor glass and the composition of the residues presents some differences. The decomposition mechanism is complex and involves concomitant processes such as elimination of $P(Ph)_2CH_2Cl_2$ radicals and Cl_2 molecules. The residues, both in the solid state and embedded in the glass, consist of a mixture of compounds such as oxides, phosphates and metallic palladium.

ACKNOWLEDGMENTS

The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Brazil) for the financial support.

RESUMO

Estudos dos complexos $Pd_2(dppm)_2Cl_2$, $Pd_2(dppm)_2(SnCl_3)Cl$ e $Pd_2(dppm)_2(SnCl_3)_2$ (dppm = bis[diphenylphosphino(methane)], $(C_6H_5)_2PCH_2P(C_6H_5)_2$) por análise termogravimétrica

(TG), no estado sólido e imobilizados no vidro poroso Vycor, são descritos. Os mecanismos de decomposição dos complexos no estado sólido e imobilizados no vidro poroso Vycor são similares e apenas uma ligeira estabilização é observada mediante a imobilização. Os produtos de decomposição foram caracterizados por difração de raios-X, espectroscopias Raman e de Refletância difusa no infravermelho, indicando a presença de uma mistura de paládio metálico e espécies oxidadas tais como PdO, fosfatos condensados, SnO_2 e SnP_2O_7. Os produtos de decomposição dos complexos imobilizados no PVG apresentaram quantidades mais elevadas de PdO do que os resíduos no estado sólido, segundo a difração de raios-X, em virtude provavelmente da ocorrência de reações com grupamentos da superfície do vidro, bem como pelo fato de que as moléculas adsorvidas se encontram isoladas umas em relação às outras.

Palavras-chave: complexos de paládio(I), vidro poroso Vycor, bis[difenilfosfino)metano, análise termogravimétrica.

REFERENCES

ALVES FL, RAIMUNDO JR IM, GIMENEZ IF AND ALVES OL. 2005. An organopalladium-PVC membrane for sulphur dioxide optical sensing. Sensors Actuators B 107: 47–52.

ANDO R, YAGYU T AND MAEDA M. 2004. Characterization of oxovanadium (IV)-Schiff-base complexes and those bound on resin, and their use in sulfide oxidation. Inorg Chim Acta 357: 2237–2244.

BALCH AL AND BENNER LS. 1982. Binuclear transition-metal complexes bridged by methylenebis(diphenylphosphine). Inorg Synth 21: 47–50.

BARBIERI RS, BELLATO CR AND MASSABNI AC. 1995. Thermal-analysis of coordination-compounds .3. thermal-decomposition of platinum complexes containing triphenylphosphine, triphenylarsine and triphenylstibine. Thermochim Acta 259: 277–286.

CHAN SS AND BELL AT. 1984. Characterization of the preparation of Pd/SiO_2 and Pd/La_2O_3 by laser Raman-spectroscopy. J Catal 89: 433–441.

EVRARD D, GROISONK, MUGNIER Y AND HARVEY PD. 2004. The $Pd_4(dppm)_4(H)_2^{2+}$ cluster: a precatalyst for the homogeneous hydrogenation of alkynes. Inorg Chem 43: 790–796.

GIMENEZ IF AND ALVES OL. 2002. Immobilisation of complexes containing metal-metal bonds in porous Vycor glass and subsequent insertion of gas molecules into the Pd-Pd bonds. Glass Technol 43C: 166–169.

GIMENEZ IF AND ALVES OL. 2004. Properties of $[Pd_2X_2(dppm)_2]$ (X = Cl, $SnCl_3$, dppm = bis(diphenylphosphino)methane) complexes on porous vycor glass. J Braz Chem Soc 15: 640–645.

GLOCKING F AND POLLOCK RJI. 1972. Novel dimeric platinum(I) complex. J Chem Soc Chem Commun 88: 467–467.

GUAN X-H, LIU Q, CHEN GH AND SHANG C. 2005. Surface complexation of condensed phosphate to aluminum hydroxide: An ATR-FTIR spectroscopic investigation. J Colloid Interface Sci 289: 319–327.

HOOD H AND NORDBERG ME. 1938. Treated borosilicate glass. US Patent 2,106,744.

HOOD HP AND NORDBERG ME. 1942. Method of treating borosilicate glasses. US Patent 2,286,275.

HUBIN R AND TARTE P. 1967. Spectre d'absorption infrarouge des pyrophosphates et pyroarseniates cubiques d'éléments tetravalents $X_6P_2O_7$ et $X_6As_2O_7$. Spectrochim Acta 23A: 1815–1815.

JCPDS – JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS FILES – International Centre for Diffraction Data.

KIRSS RU AND EISENBERG R. 1989. Di(phosphine)-bridged complexes of palladium – parahydrogen-induced polarization in hydrogenation reactions and structure determination of tris(μ-bis(diphenylphosphino)methane)dipalladium, $Pd_2(dppm)_3$. Inorg Chem 28: 3372–3378.

KURESHY RI, KHAN NUH AND ABDI SHR. 2004. Dicationic chiral Mn(III) salen complex exchanged in the interlayers of montmorillonite clay: a heterogeneous enantioselective catalyst for epoxidation of nonfunctionalized alkenes. J Catal 221: 234–240.

LEE C-L, YANG Y-P, RETTIG SJ, JAMES BR, NELSON DA AND LILGA MA. 1986. Synthesis and characterization of dinuclear palladium(I) and mononuclear palladium(II) complexes containing 1,1-bis(diphenylphosphino)ethane (dpmMe) and related mixed-ligand complexes containing dpmMe with either bis(diphenylphosphino)methane (dpm) or 2-(diphenylphosphino)pyridine (Ph_2Ppy) – X-ray crystal-structures of $PdCl_2(dpmMe)$ and $Pd_2Cl_2(\mu\text{-}dpmMe)_2$. Organomet 5: 2220–2228.

MACEDO JS, OTUBO L, FERREIRA OP, GIMENEZ IF, MAZALI IO AND BARRETO LS. 2008. Biomorphic activated porous carbons with complex microstructures from lignocellulosic residues, Microporous Mesoporous Mater 107: 276–285.

NGUYEN DH, COPPEL Y, URRUTIGOITY M AND KALCK P. 2005. $[Pd(H)(SnCl_3)L_2]$: The key active species in the catalyzed alkoxycarbonylation reaction of terminal alkenes. J Organomet Chem 690: 2947–2951.

OLMSTEAD MM, BENNER LS, HOPE H AND BALCH AL. 1979. Addition of tin(II) chloride to $Pd_2(Ph_2PCH2PPh_2)_2Cl_2$ – Crystal and molecular-structure of $Pd_2(Ph_2PCH_2PPh_2)_2(SnCl_3)Cl$. Inorg Chim Acta 32: 193–198.

RICHMOND MK, SCOTT SL, YAP GPA AND ALPER H. 2002. Preparation of dinuclear phosphine-bridged palladium(II) species and their silica-bound analogues as catalysts for the cyclization of aminoalkynes. Organomet 21: 3395–3400.

SILVA KRB, RAIMUNDO JR IM, GIMENEZ IF AND ALVES OL. 2006. Optical sensor for sulphur dioxide determination in wines. J Agric Food Chem 54: 8697–8701.

SUNIL D, SOKOLOV J, RAFAILOVICH MH, DUAN X AND GAFNEY HD. 1993. Evidence for the photodeposition of elemental iron in porous vycor glass. Inorg Chem 32: 4489–4490.

YANG Y AND MCELWEE-WHITE L. 2004. Electrochemical oxidation of methanol using dppm-bridged Ru/Pd, Ru/Pt and Ru/Au catalyst. Dalton Trans 15: 2352–2356.

ZAYED MA, ARIFIEN AESA AND HASSAN FSM. 1999. Investigation of complexes of diphenyl-phosphine derivatives by thermal and other physicochemical methods of analyses. J Thermal Anal 55: 205–212.