ADSORPTION ESSAYS OF PALLADIUM IN MODIFIED SILICA GEL WITH THIOURONIUM GROUPS: EXPERIMENTAL AND THEORICAL STUDIES

Dedicated in memory of Dra. Ana María Leiva Maturana

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ABSTRACT

The silylant 3-cloropropyltriethoxysilyl was anchored over silica gel in anhydrous conditions in order to react with thiourea to obtain modified silica gel with thiouronium. The aim to obtain an inorganic support that is able to hijack metals from the VIII group such as palladium. The product was characterized by S_{BET} and FTIR infrared spectroscopy. For the determination of the structure in the modified silica gel NMR spectra of silicon and carbon were preformed in solid state. The coordination form of the modified silica gel to the metal was studied computationally in the context of the DFT theory, using the ADF code. This was a collaborative work with *"Fundación Chile"* for the recuperation of precious metals from the mining industry.

Keywords: silica gel, functionalization, coordination agents.

INTRODUCTION

The objective of this work is to restore the minerals with added value that are used in the process of the Chilean mines by giving them a third treatment, implementing a modified inorganic support with an organic chain with coordinated groups [1-3]. The thiouronium group has been used in organic resins for the recuperation of metals with added value [4-8].

The modification of inorganic supports, such as silica gel, has been often used in the areas of heterogeneous catalysis, ionic chromatography and chemisorption of metals of interest [9-13] and in several industrial applications [14-16], because of its chemical stability towards extreme pH conditions and temperature. Silica gel is an inorganic support constituted by a skeleton of silicon and oxygen, whose union is called siloxans Si-O-Si. These bonds are randomly distributed establishing a great number of silanols Si-OH [17-18].

These groups are distributed on the surface in three different ways: free, geminals and local, being mainly found hydrated by water molecules adsorbed by hydrogen bridges, see Figure 1.
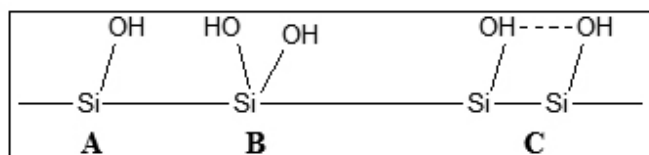

Figure 1: *Different forms of the distribution of the silanols groups on the surface of the silica gel: (A) Free, (B) Geminals and (C) local*

The modification of the surface of silica gel has the objective to link in one material the properties of an inorganic support with an organic chain. This process is known as functionalization [19-21].

The reagents used for this purpose are called sililants agents, which are represented as $(Y)_3$-Si-RX, where Y is an alcoxy group and X represents a functional group of the chain (Cl, SH, NH_2, etc) and R is a radical. According to the literature, the most reproducible synthesis route is one in which the reaction made in an anhydrous condition [22-23]. This is why it is necessary to withdraw all the water molecules adsorbed, process that is known as activation, and to use an anhydrous dissolvent with a high boiling point. Other authors have proposed that the free silanols groups are those that react with the sililant

agent and the most common bond belongs to the type mono and bidentate [24-25], figure 2.
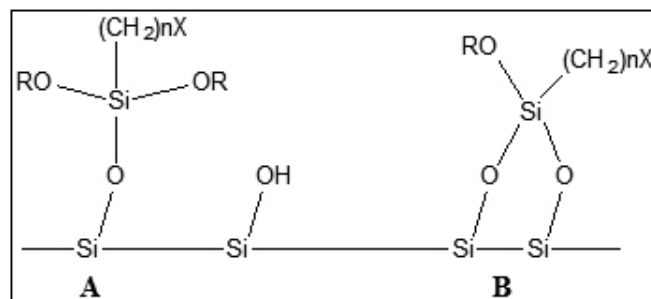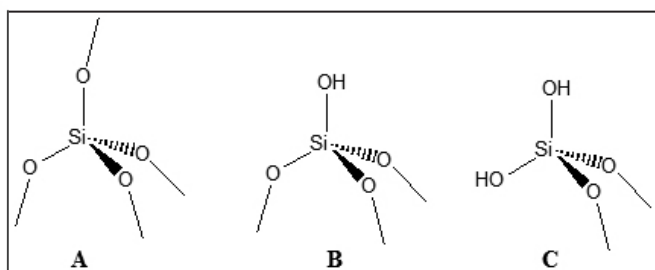

Figure 2: *Different types of the sililants agents union in the surface of the silica gel: (A) mono dentate and (B) bidentate*

The characterization of the modified surface is performed with techniques like S_{BET} (Brunauer-Emmett-Teller isotherm) [26], which estimates the surface of a solid, elemental analysis and combined FTIR [27-29] and RMN solid state techniques [30-31], which provide a good characterization of the product.

The vibrations of the free silanols group may be appreciated by the FTIR spectra. The Si-OH vibrations in the silica gel appear as signals at 3600.0 and 970.0 cm^{-1} whose disappearance confirms the modification of the silica gel [32]

In the ^{29}Si NMR study three types of signals can be distinguished that use the Q^n nomenclature, which represents the n atoms of silicon that are linked in the structure. In the silica gel, a peak associated to the geminal silanols groups is assigned as Q^2 and appears near – 90.0 ppm. The simple silanols groups are assigned as Q^3 at -100.0 ppm, and the siloxans Si-O-Si group is assigned as Q^4 at -110.0 ppm [30-31], being the main group in the structure (Figure 3).

Figure 3: Q^n *nomenclature used in the designation of different types of groups in the silica gel: (A) Q^4, (B) Q^3 and (C) Q^2.*

The substitution of the silanols groups can also be observed in the Si-C union, whose nomenclature is assigned as T^n. When the modification of the silica gel surface occurs, its structure changes and new signs of a chemical shift of 45.0 ppm appear. These unions can be assigned as T^3 nearby -65.0 ppm and T^2 at -55.0 ppm [26-27], figure 4.
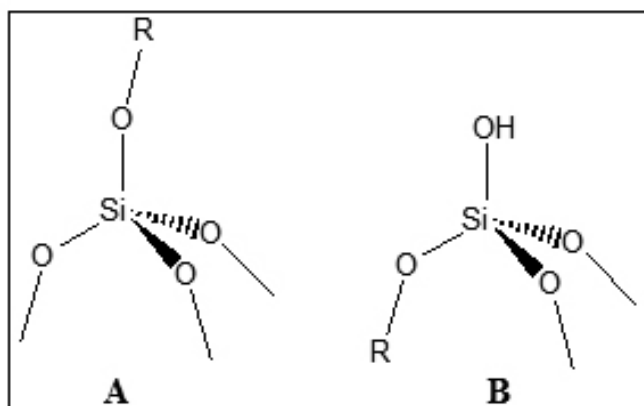
Figure 4: T^n *Nomenclature use for the designation of the different modifications on the surface of the silica gel: (A) T^3 and (B) T^2.*

The modified of the silica gel with the thiouronium group from the modified silica with the 3-chloropropyl group and thiourea provide a cheaper support in order to make a gradual upgrade to a bank level for the recovery of the metals, along with a chemical process that allows this recovery [32-35], presenting the development of new technologies at a low price.

Computational studies were performed in the framework of the theory of functional density [36], in order to propose a coordination model to the studied metal, whose analysis of the internal energy structure allows formulating a criterion to discern the coordination formula.

EXPERIMENTAL

All the chosen starting materials were purchased from Merck, Winkler and Aldrich.

The source of the silica gel 60 used in this study is Merck, with a particle size of 0.063 – 0.200 mm (70 - 230 mesh), a surface of 463 m^2 g^{-1} and a pore diameter of 63.9 Å.

The infrared spectra were measured in a Bruker model vector 22 equipment. The Nuclear magnetic resonance (NMR) for the solid sample was performed in a Bruker AMX 300 equipment. The used frequency was 300 MHz with 7.4 T, 5 µ of pulse and a contact time of 5 ms, the repetition number was 15 k and the magic angle 54.7°. As the reference solid sodium 4.4-dimethyl-4-silopentanesulfonate was used in all the cases as an internal standard. The surface area S_{BET} was obtained using Flowsorb II 2300 Micromeritics Instruments.

Preparations.

Inorganic support. Silica Gel 60 (Merck), was dry under vacuum by 8 hours at 443 K.

S_{BET} 463.0 m^2 g^{-1}, Porous diameter 63.90 Å. Elemental analysis 0,00 % C, 0.60 % H. FTIR (cm^{-1}): 3696.9 (υ Si-OH free silanol), 3452.0 υ (Si-OH geminal silanol), 1637.5 υ (H_2O), 1097.5 υ (Si-O-Si), 972.5 (Si-OH free silanol), 800.0 υ (Si-O-Si), 470.3 δ (Si-O-Si). ^{29}Si NMR solid state (δ ppm): -113.0 (Q^4) and -102.0 (Q^3).

3-cloropropyl functionalized silica gel. Silica Gel 60 (100 g) was dissolved in dry xylene (300 mL) and added 3-Cloropropyltriethoxysilane (60 mL , 0.2581 mol) and mixture under nitrogen by 72 hours with mechanical stirred. Cooling at room temperature and filter the mixture and washed by xylene and acethone. Dry under vacuum by 8 hours. Yield: 99,1 g (99.0 %). Elemental analysis 6.49 % C, 1.28 % H. S_{BET} 380,8 m^2 g^{-1}, Porous Diameter 39.60 Å. FTIR (cm^{-1}): 2983,7 ; υ (CH_2), 1637,8 ; υ (H_2O), 1097.1 υ (Si-O-Si) ; 802.7 υ (Si-O-Si); 468.6 δ (Si-O-Si).

3-isothiouroniumpropyl functionalized silica gel. 40 g of 3-chloropropyl functionalized silica gel was dissolved in mixture dry xilene (150mL). Added Thiourea (2g, 0.0253 mol) disolved by dry acethone. The mixture was refluxing under nitrogen by mechanical stirring by 36 hours. The product was filtred and washed by methanol and acetone and dry under vacuum by 8 hours. Yields: 39,0 g (97.5 %). Elemental analysis: 5.69 % C, 1,11 % H, 3.13 % S , 0,84 % N. S_{BET} 388.0 m^2 g^{-1}, Diameter 41.79 Å. FTIR (cm^{-1}): 3448.7 υ (Si-OH geminal silanol) ; 2361.7 υ (C-S); 1637.4 υ (H_2O); 1096.5 υ (Si-O-Si); 804.9 υ (Si-O-Si) and 468.7 δ (Si-O-Si). ^{29} Si NMR solid state (δ ppm): -112.3 (Q^4); -104.949 (Q^3); -103.22 (Q^2); -68.7 (T^3). ^{13}C NMR solid state (δ ppm): 59.45 (-OCH_2-); 48.80 (S-C($NH_2)_2$); 38.33 (Si-CH_2-); 29.29 (-CH_2-); 16.33 (-CH_3); 11.15 (-CH_2-S-).

Adsorption Curves
The adsorption essays were preformed with a Horizon Ecology Co. peristaltic pump, Chicago, ILL60648 model with Perkin Elmer head, model 7015-21, and Masterflex 96410-15 hoses. The vertical glass column used had a height of 28 [cm], an internal diameter of 1.5 cm and a volume capacity of 38 mL. In the essays, 0.20- 0,15 g of silica gel modified with 3-thiouroniumpropyl and 58.6 g of quartz stone were used. A flow of 4.28 mL /min were used and samples were taken every 20 mL. We used a model dissolution of 150 mL of acid Palladium (II) tetrachloride (84 mg / L), dissolution pH of 2.7 and 12.4 °C of temperature [37]. Each aliquot was measured by Atomic Absorption technique.

COMPUTATIONAL DETAILS.

All of the calculations for the coordination models of the modified silica gel with 3-thiouroniumpropyl and palladium were performed using the ADF code, using as the TZ2P basis set with the LDA and BP86 functionals [38-41].

RESULTS AND DISCUSSIONS

1. Silica gel modification.
The modified silica gel with 3-cloropropyl group and with the 3-thiouroniumpropyl group were synthesized in anhydrous conditions according to scheme 1.
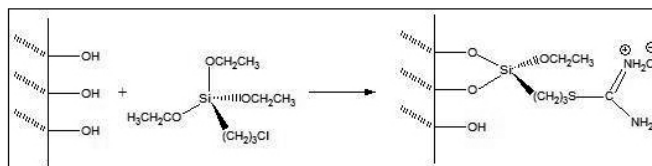
Scheme 1.

Some general properties of the unmodified silica gel and the modified ones with the above mentioned groups are detailed in table 1. The modification of the silica gel matrix shows a decrease in the superficial area in relation with the unmodified silica gel matrix, being observed the values of the superficial area of 463.6 m^2 g^{-1} for the unmodified silica gel and of 388.0 m^2 g^{-1} for the silica gel with the thiouronium group. This decrease is attributed to the difficulty of the

nitrogen gas to reach the pores of the modified matrix in the S_{BET} experiment, which would be a qualitative proof of the modification of the surface [13-17].

The FT-IR signal of the free silanol group present in the unmodified silica gel appears at 3696.9 cm^{-1}. It is observed that it disappears when it is modified by the chloropropyl and thiouroniumpropyl groups, respectively. Moreover, the assignment of all the absorption characteristics in the FT-IR of the organic groups is fairly difficult to assign due to the high intensity of the silica gel signals, where the vibrations of the C-H groups are being maske. Some of the observed stretching frequencies are comparable to those frequencies obtained through the frequency analysis of the optimized structures those are shown between parenthesis in table 1.

Table 1. *Some general properties of the silica gel 60, 3-chloropropyl and 3-thiouronium propyl modified silica gel.*

Property	Silica gel 60	3-Cloropropyl functionalized silica gel (1)	3-Thiouronium-propyl functional-ized silica gel (2)
Area / m2 g-1	463.6	380.8	388
Porous diameter / Å	48.34	39.6	41.79
υOH free silanol / cm $^{-1}$	3696.9	---	---
υOH Geminal silanol / cm $^{-1}$	3452	3448.9	3448.7
υOH water / cm $^{-1}$	1637.5	1637.8	1637.4
υAsimetric Si-O-Si / cm $^{-1}$	1097.5	1097.1	1096.5
υSiOH free silanol / cm $^{-1}$	972.5	---	---
υSimetric Si-O-Si / cm $^{-1}$	800	802.7	804.9
δ Si-O-Si cm $^{-1}$	470.3	468.6	468.7
υC-Cl / cm $^{-1}$	---	(228)	---
υCH$_2$ / cm $^{-1}$	---	2983.7 (2956;2982;2985)	(2931;2949;2979)
υNH$_2$ / cm $^{-1}$	---	---	(3345;3367;3445)
υC-S / cm $^{-1}$	---	---	2361.7

The solid spectra of the solid state ^{29}Si NMR for the unmodified silica gel showed two peaks in -113 and -102 ppm assigned to Q^4 and Q^3 . The ^{29}Si-NMR spectra of the group 3-thiouroniumpropyl modified silica gel showed a peak in -105.14 ppm assigned to Q^3 and a new peak at -68.7 ppm assigned to T^3 [30-32].

To be able to achieve a fair characterization of the modified silica gel, numbers from 1 through 6 were assigned to the carbon present in the thiouroniumpropyl group, figure 5. The solid state ^{13}C-NMR spectra of the thiouroniumpropyl group modified silica gel present various peaks at 11.15, 29.29 and 38.33 ppm, assigned to the carbon atoms 1,2 and 3. Another peak at 48.80 ppm was assigned to carbon 6 and two peaks at 59, 45 and 16.33 ppm assigned to carbons 4 and 5 of the ethoxy groups (Figure 5).
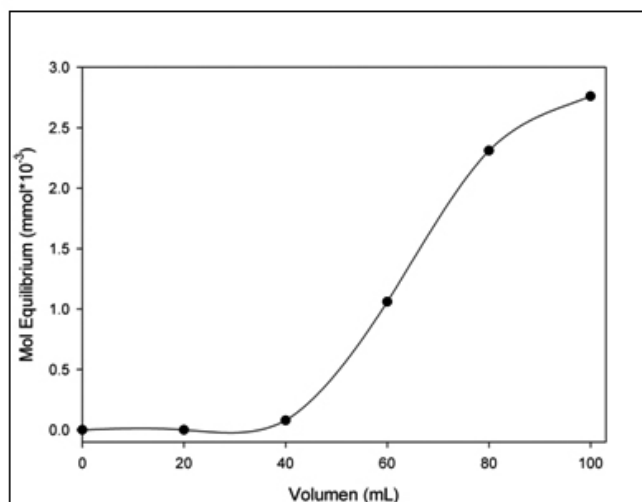
$$(H_3C-H_2CO)_3-Si-CH_2-CH_2-CH_2-S-CN_2H_4Cl$$
$$\quad 5 \quad\quad 4 \quad\quad\quad 3 \quad\quad 2 \quad\quad 1 \quad\quad\quad 6$$
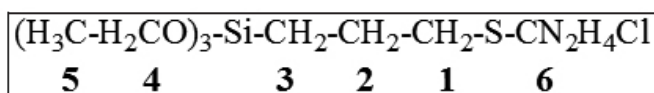
Figure 5: *Assignment of the carbon atoms for the NMR solid spectrum analysis.*

2. Adsorption Tests.

The elemental analysis for sulfur in the thiouroniumpropyl group of modified silica gel was of 3.1286 %. Based on this found percentage, the modification degree for the modified silica gel matrix was 0.9758 mmol of sulfur per gram.

To study the adsorption capabilities of the modified silica gel, ideal solutions of Pd (II) of 0.7894 mol/L of concentration were analyzed. It was placed in contact with the column with 0.16 g of modified silica gel, 100 mL of Pd(II) solution; 20 mL aliquots and that were analyzed by atomic absorption for their palladium concentration. An adsorption graphic was obtained showing a deformed "S"shape, figure 6. From this figure an inflection point can be observed when around 60 mL of solution were passed through the column, which is in a saturated stage because of the metal. When the first 100 ml of the Pd(II) solution had passed there was a pre concentration of 0.0727 mmol of Pd(II) in the column, corresponding to a 92% of recovery, figure 6.
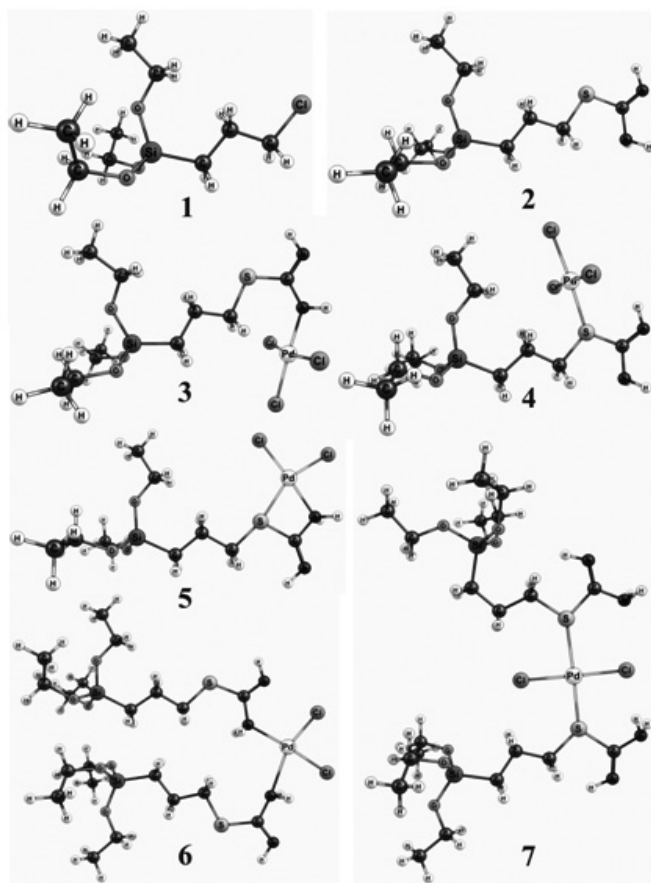
Preliminary elusion essays of Pd(II) with 100 ml of 0.1 M NaCN solution at a pH=12 showed that, more than 25% of the studied metal was recovered. It has to be mentioned that the elusion study of the metal is still in an experimental phase, employing other basic soft coordinating agents according to Pearsons definition [37].

Figure 6: *Palladium adsorption essay in thiouronium modified silica gel.*

3. Computational Study

To complete the study of the interaction form between the Pd(II) and the modified silica gel, a computational calculation was made in the framework of the DFT density functional theory over five coordination proposed models, figure 7. [38-42].

that are directly coordinated with the metal and also show a larger electrostatic interaction, when comparing the models 6 and 7.

Table 2. *Bonding energy decomposition analysis by fragments (Pd + rest to systems) for all compounds in (kcal*mol-1).*

Compounds	Eb	ΔE_{Pauli}	ΔE_{Elstat}*		ΔE_{Orb}*	
3	-24.28	106.69	-92.31	(70.5)	-38.66	(29.5)
4	-16.09	90.97	-66.50	(62.1)	-40.56	(37.9)
5	-35.20	119.91	-102.34	(66.0)	-52.77	(34.0)
6	-26.12	95.80	-78.37	(64.3)	-43.55	(35.7)
7	-49.76	179.89	-110.34	(48.1)	-119.31	(52.0)

*Between parentheses the porcentual stabilizing energy, DE_{Elstat} and DE_{Orb} is presented.

The experimental values obtained by successive essays show that the amount of thiouronium 0.16 g modified silica gel correspond to 0.1561 mmol of the thiouronium group. The adsorbed Pd (II) amount is equal to 0.0789 mmol, with a thiouronium/Palladium molar proportion of 2/1. Such a result suggests that the model 7 coordination is the most adequate coordination of the Pd (II) modified silica gel.

CONCLUSIONS

The thiournonium propyl modified silica gel was synthesized in anhydrous conditions and characterized using the above mentioned techniques. The palladium coordination over the modified silica gel matrix was studied by means of adsorption essays and completed with the theoretical studies showing that the most likely coordination model could be through sulfur or hydrogen in the thiouronium group, the modified silica gel/Pd (II) relation 2/1, being the model 7 the most likely. Since the thiournonium group modified silica gel and the adsorbed Pd (II) do not show an ionic interaction due to the stability of the adsorbed metal toward pH variations [7-8] that mechanism was discarded.

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Figure 7: *Molecular structure of the 1 and 2 compounds, and of the proposed coordination models for this study 3-7.*

All of the results shown were made with the ADF2008 [43] code. The relativistic scalar effects were incorporated using zeroth order regular approximation (ZORA- Zeroth Order Regular Approximation) [44-46] . All the structures were optimized by the analytic energy gradient approximation techniques, put into practice by Verluis and Ziegler [47] , which employs the local density approximation (LDA) [48] and the generalized gradient approximation (GGA) and the functional BP86 [49-50]. The basis triple-z set was also used along with the double polarization functions (TZ2P) [51] . The frequency calculations were made with the second derivative optimized geometry method of the total energy regarding the internal coordinates, put into practice in the ADF code.

The interaction energy decomposition E_{Int} was made as proposed by Morokuma and Ziegler [52-54]. This energy can be divided into three main components:

$E_{Elstatis}$ the electrostatic component that is calculated by the superposition of the fragment density imposed in the molecular geometry, which corresponds to the classical electrostatic effects associated with the Coulombic attraction and the repulsion. The Pauli energy E_{pauli} are the repulsive interactions caused by the fact that two electrons with the same spin cannot occupy the same spatial region.

The orbital energy E_{Orb} is the interaction orbital term that is stabilized. Therefore, the total energy is:

$$\Delta E_{Int} = \Delta E_{Pauli} + \Delta E_{Elstat} + \Delta E_{Orb}$$

These relative energies for the five proposed models are shown in Table 2. The studies show that the binding energies for the models 5 and 7 present the most stable energy values. The model 5 presents a specter stabilization contribution of electrostatic energy. The model 7 shows an interaction between the silica gel and the Pd metal and shows a larger contribution in percentage of the orbital energy. It is plausible that in the model 6, the modified silica gel interaction with the metal is not as stable as in the model 7 due to the observed less relaxation in the chains and the smaller angle between atoms

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