

Matrix Effect on Electrochemical Properties of $[\text{Co}(\text{sepulchrate})]^{3+}$ Immobilized on Silica Gel and Modified Silica Gel Surfaces

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O complexo $[\text{Co}(\text{sepulchrato})]^{3+}$ imobilizado sobre a superfície de sílica gel, $\text{Sil}-[\text{Co}(\text{sepulchrato})]^{3+}$, sílica gel quimicamente modificada com óxido de zircônio(IV), $\text{SilZr}-[\text{Co}(\text{sepulchrato})]^{3+}$, e sílica gel quimicamente modificada com fosfato de zircônio(IV), $\text{SilZrP}-[\text{Co}(\text{sepulchrato})]^{3+}$, apresentou resposta eletroquímica correspondente ao processo redox Co(III)/Co(II) .

The $[\text{Co}(\text{sepulchrato})]^{3+}$ complex immobilized on the silica gel surface, $\text{Sil}-[\text{Co}(\text{sepulchrato})]^{3+}$, silica gel chemically modified with zirconium(IV) oxide, $\text{SilZr}-[\text{Co}(\text{sepulchrato})]^{3+}$, and silica gel chemically modified with zirconium(IV) phosphate, $\text{SilZrP}-[\text{Co}(\text{sepulchrato})]^{3+}$, showed electrochemical responses due to the redox process of the couple Co(III)/Co(II) .

Keywords: silica gel, zirconium phosphate, cobalt sepulchrato complex, chemically modified silica gel

Introduction

Silica gel is a solid commonly used as the supporting matrix for various substrates, due to its high chemical and thermal stability as well as its high mechanical resistance. Therefore, various reports concerning chemical modifications of the silica gel surfaces with oxides, metal complexes, organic molecules and organometallic compounds have been described in the literature¹⁻⁵.

In recent years, studies on the immobilization of electroactive species on chemically modified silica have also been published⁶⁻⁸. The main interest has been to investigate the electrochemical properties of these materials as electrochemical sensors and in electrocatalyzed reactions^{9,10}.

Cobalt macrobicyclic complexes, in particular [(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) cobalt(III)]³⁺, $[\text{Co}(\text{sepulchrato})]^{3+}$ ¹¹⁻¹⁵, show high chemical stability. The redox reaction of the couple Co(III)/Co(II) is reversible, in contrast to that observed for $[\text{Co}(\text{NH}_3)_6]^{3+}$, which under reduction have their ligands replaced very quickly by solvent molecules¹⁶. The kinetics of electron transference is also considerably faster for the sepulchrato complex¹⁷.

Zirconium oxide or zirconium phosphate in the bulk phase are cationic exchangers^{18,19}, and in the second case in particular, present a strong acidic character²⁰. Both substrates were immobilized on a silica gel surface and $[\text{Co}(\text{sepulchrato})]^{3+}$ was adsorbed by an ion exchange reaction. The electron transfer behavior of the adsorbed complex was compared with that of the complex adsorbed on a silica surface.

In this work, the matrix effect on the electrochemical behavior of the complex $[\text{Co}(\text{sepulchrato})]^{3+}$, immobilized on silica gel, and on silica gel chemically modified with zirconium(IV) oxide and zirconium(IV) phosphate, is reported.

Experimental

Modification of silica gel

Preparation of SilZr

Silica gel, having a specific surface area of $S_{\text{BET}} = 500 \text{ m}^2\text{g}^{-1}$, was previously activated by heating at 423 K under vacuum (10^{-3} Torr). About 50 g of this material was immersed in 300 cm³ of dry ethanol, and 11.6 g (0.05 mol) of ZrCl_4 was added. The mixture was refluxed for 8 h under nitrogen. The solid was filtered under nitrogen in a Schlenk apparatus, washed with pure ethanol and then heated at 400 K under vacuum. The resulting solid was immersed in bi-distilled water, washed until all of the chloride ions were eliminated, and then dried in an oven at 400 K.

Preparation of SilZrP

About 20 g of SilZr was immersed in 200 cm³ of an aqueous solution of 0.1 M H_3PO_4 , and the mixture was shaken for 8 h. The solid was washed and filtered. The obtained material was refluxed for 6 h with 5.8 g (0.02 mol) of ZrOCl_2 in 100 mL of water, washed and filtered. The resulting solid was then immersed in 0.1 M H_3PO_4 over-

night, washed with water, filtered and dried in an oven at 400 K. The amount of zirconium was determined by X-ray fluorescence analysis, and the quantity of phosphorus was determined by the spectrophotometry technique.

Adsorption of $[Co(sepulchrate)]^{3+}$ on the matrix surface

Silica gel, SilZr and SilZrP were initially washed with 0.1 M $NaHCO_3$ solution. The solids were washed with water in order to eliminate the excess of electrolytes. About 0.2 g of each solid sample was immersed in 10 cm³ of 0.01 M of Cobalt(III) sepulchrate tris(tetraphenylborate) water-ethanol (50% v/v) solution. The mixture was stirred for 5 min, and the solid was filtered, washed and dried under vacuum at room temperature. The quantity of cobalt was analyzed by X-ray fluorescence analysis.

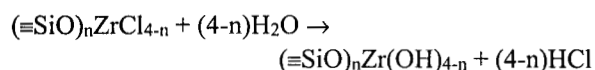
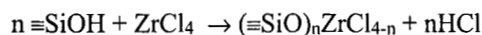
Cyclic voltammetry (CV)

The carbon paste electrodes (working electrodes) were prepared by mixing 40 mg of the material with 30 mg of graphite (Fluka) and a small amount of paraffin oil. A saturated calomel electrode (SCE) was used as a reference electrode, with a platinum wire as the auxiliary electrode. All the measurements were carried out in a pure nitrogen atmosphere.

Results

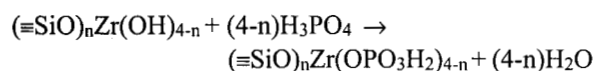
Preparation and characteristics of the material

The reaction of $ZrCl_4$ with silica gel and the further hydrolysis can be represented by the following equations:



where $\equiv SiOH$ stands for the silanol groups on the silica surface.

The resulting solid is immersed in phosphoric acid solution and the reaction can be represented by the following equation:



where $(\equiv SiO)_n Zr(OH)_{4-n}$ and $(\equiv SiO)_n Zr(OPO_3H_2)_{4-n}$ are the previously mentioned SilZr and SilZrP, respectively.

Adsorption of $[Co(sepulchrate)]^{3+}$ by Sil, SilZr or SilZrP occurs by the exchange reaction of the cation with the proton of the hydroxyl group of the three solids. In this case, the order of acidity is $SilZrP > SilZr > Sil$. The quantities of the chemical species on the silica gel surface determined by chemical analysis are presented in Table 1.

Table 1. Chemical analysis of Sil-Co(sep), SilZr-Co(sep) and SilZrP-Co(sep).

Matrix	Zr/ $\mu\text{mol g}^{-1}$	P/ $\mu\text{mol g}^{-1}$	Co/ $\mu\text{mol g}^{-1}$
Sil-Co(sep)	—	—	17
SilZr-Co(sep)	317	—	16
SilZrP-Co(sep)	535	123	30

The larger amount of the cobalt complex on the SilZrP matrix is due to the higher acidity of this material.

In order to abbreviate the notations, $[Co(sepulchrate)]^{3+}$ adsorbed on the matrices will hereafter be denoted as Sil-Co(sep), SilZr-Co(sep) and SilZrP-Co(sep).

Cyclic voltammetry

Figure 1a shows the cyclic voltammogram of SilZrP-Co(sep). The cyclic voltammograms of Sil-Co(sep) and SilZr-Co(sep) are almost the same and thus, they are not shown here. No current enhancement is observed for SilZrP cycled in similar conditions, as illustrated in Fig. 1b.

The electrochemical stability of the electroactive species under various potential cycling is illustrated in Fig. 2. After 200 cycles the decrease of peak currents are approximately 60 and 70% of the initial current intensity for I_{pc} (cathodic peak current) and I_{pa} (anodic peak current), respectively.

The main electrochemical parameters, obtained for SilZrP-Co(sep) under various scan rates, are presented in Table 2. The results obtained for Sil-Co(sep) and SilZr-Co(sep) were again almost the same as those obtained for SilZrP-Co(sep). An increase in the separations of the peak to peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively) as the scan rates increase, are observed. In order to have information about the nature of the electron transfer process at the solid-solution interface, I_{pc} was plotted against $v^{1/2}$ (Fig. 3), where v is the scan rate.

Figure 4 presents the effect of the pH solution on the mid-point potentials $E_{1/2}$ [$E_{1/2} = (E_{pa} + E_{pc})/2$] for different

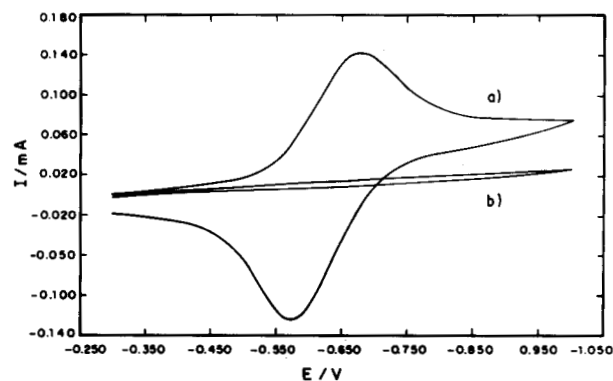
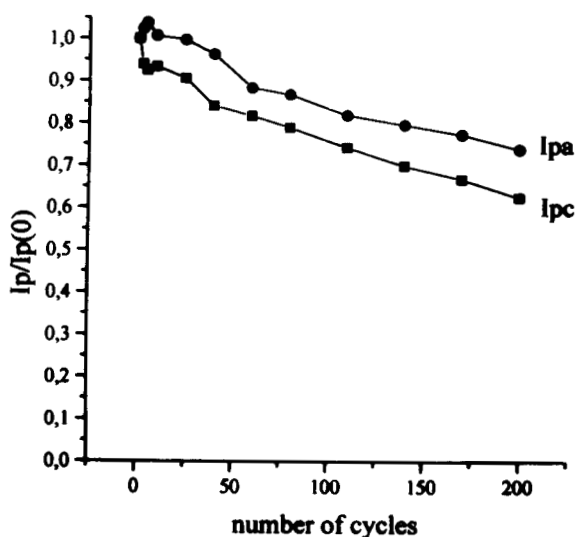


Figure 1. Cyclic voltammograms of: a) SilZrP-Co(sep) and b) SilZrP; supporting electrolyte: 1 M NaCl, pH 5.5; scan rate: 10 mVs⁻¹.

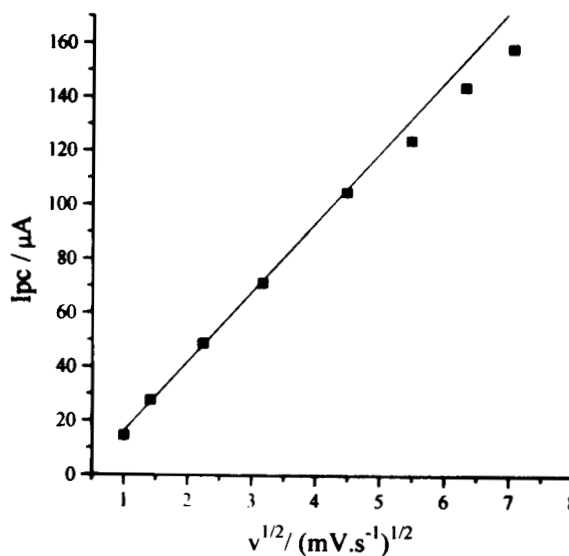
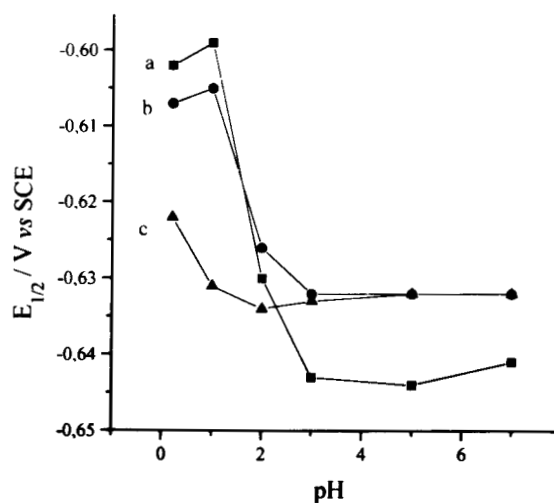
Table 2. Electrochemical parameters of SilZrP-Co(sep).

$v / \text{mV s}^{-1}$	$I_{pa} / \mu\text{A}$	$I_{pc} / \mu\text{A}$	$\Delta E_p / \text{V}$	$E_{1/2} / \text{V}$
1	19	14	0.038	-0.585
2	33	27	0.058	-0.583
5	61	48	0.082	-0.579
10	82	71	0.104	-0.578
20	111	104	0.126	-0.577
30	131	124	0.140	-0.578
40	152	143	0.152	-0.578
50	168	158	0.160	-0.578

Supporting electrolyte: 1 M NaClO_4 , pH 5; v = scan rate.**Figure 2.** Decrease in anodic (I_{pa}) and cathodic (I_{pc}) peak currents as a function of number of cycles. I_p is the peak current and $I_p(0)$ is the initial peak current; supporting electrolyte: 1 M NaClO_4 , pH 5.5; scan rate: 10 mV s^{-1} .

matrices. The solutions were prepared at the desired pH from HCl and NaOH solutions to maintain the ionic strength constant. Between pH 3 and 7, for Sil-Co(sep) and SilZr-Co(sep), $E_{1/2}$ remains practically constant, while at $\text{pH} < 3$ a shift towards more positive values is observed. For SilZrP-Co(sep) the values of $E_{1/2}$ remain practically constant for solutions between pH 1 and 7. A small shift toward a more positive potential is observed at pH 0.

The nature and concentration of the supporting electrolytes can also have an effect on the $E_{1/2}$ values. For instance, increasing the NaOAc supporting electrolyte concentration from 0.1 up to 2 M, the mid-point potential shifts approximately 120 mV toward more negative values for Sil-Co(sep), 100 mV for SilZr-Co(sep) and 80 mV for SilZrP-Co(sep). Using NaCl as the supporting electrolyte, the observed shift toward more negative potentials are 60 mV for Sil-Co(sep), and 50 mV for SilZr-Co(sep), while no potential change is observed for SilZrP-Co(sep). In

**Figure 3.** I_p vs. $v^{1/2}$ for SilZrP-Co(sep), where v is the scan rate and I_{pc} is the cathodic peak current. Supporting electrolyte: 1 M NaClO_4 , pH 5.5.**Figure 4.** Variation of $E_{1/2}$ as a function of pH of the supporting electrolyte solutions. Sil-Co(sep) (a), SilZr-Co(sep) (b) and SilZrP-Co(sep) (c); supporting electrolyte: 1 M NaCl; scan rate: 10 mV s^{-1} .

contrast, using NaClO_4 as the supporting electrolyte, a change of 30 mV in mid-point potentials to more positive values are observed for SilZrP-Co(sep) only (Fig. 5).

Discussion

The exchange capacity of Co(sep) in SilZrP is approximately twice that observed for Sil and SilZr. These results are similar to those observed for bulk-phase zirconium(IV) phosphate, which is a stronger ion exchanger than ZrO_2 or SiO_2 ¹⁸. However, the adherence of the complex on the surface of the three matrices was the same, as shown by cycling the potential about 200 times (Fig. 2). Increasing

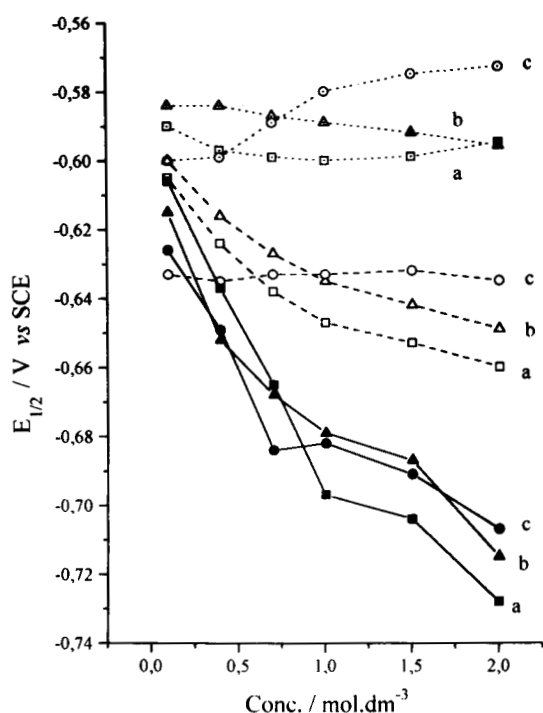
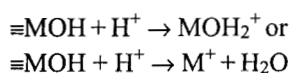


Figure 5. Change of $E_{1/2}$ as a function of supporting electrolyte concentrations. Sil-Co(sep) (a), SilZr-Co(sep) (b) and SilZrP-Co(sep) (c). Supporting electrolytes: NaOAc (—), NaCl (---) and NaClO₄ (.....).

the scan rates, the electrochemical parameters were nearly the same for Co(sep) adsorbed on the three matrices. As is presented in Table 2, the change of values of ΔE_p clearly indicates that the redox process may be controlled by (i) diffusion of the ions at the interface, and (ii) the insulating character of the surface. Plotting I_{pc} against $v^{1/2}$, a linear relationship is observed for scan velocity up to 20 mV s⁻¹. This behavior is similar to that of diffusion controlled processes²¹. At higher velocity, the deviation from linearity is presumably due to the slower electron transfer process on the surface of the porous oxides and the insulating character of the materials, as was pointed out above.

The electrochemical behavior of the adsorbed complex on the matrices is affected as the pH of the solutions as well as the nature and concentration of the supporting electrolytes are changed. In the present case the metal ion is encapsulated, and thus the shift in the $E_{1/2}$ is associated with a change in charge density of the nitrogen donor atoms coordinated to the metal. At lower pH, the surface can be protonated according to the reactions²²:



The decrease in the negative charge of the surface can decrease the electron density in the complex environment shifting $E_{1/2}$ toward more positive values. This effect is

clearly observed for Sil-Co(sep) (Fig. 4a) and SilZr-Co(sep) (Fig. 4b) as the pH of the solution decreases, while for SilZrP-Co(sep) (Fig. 4c) this effect is smaller. For $(\equiv\text{SiO})_n\text{Zr}(\text{OPO}_3\text{H}_2)_{4-n}$ the bound phosphate group is a stronger Brønsted acid than $\equiv\text{MOH}$ (M= Si or Zr)²⁰, and thus the surface is less protonated than for Sil or SilZr.

The nature of the counterion of the supporting electrolyte can also affect the mid-point potentials of Co(sep) adsorbed on the matrices. Figure 5 shows the variation of $E_{1/2}$ with concentrations of the supporting electrolytes AcO⁻, Cl⁻ and ClO₄⁻. A larger shift toward more negative potentials is observed for AcO⁻, followed by Cl⁻ and ClO₄⁻, as the concentrations are increased from 0.1 up to 2.0 M. A possible explanation for this observation is related to the interaction of the anion with the adsorbed Co(sep), since the electron donor property increases according to the order ClO₄⁻ < Cl⁻ < AcO⁻²³. An increase of the electron density of the complex by an ion pair interaction and hydrogen bond formation^{14,17} should decrease the redox potential of the couple Co(III)/Co(II). In the SilZrP matrix the $E_{1/2}$ is less affected because the interaction between the complex and the supporting electrolyte anion is inhibited by the more negatively charged surface.

Conclusions

Changes in the pH values of the solutions can change the surface charge density by protonation and thus shift the mid-point potentials to more positive values. Acidity of the immobilized zirconium phosphate is higher than that of $\equiv\text{MOH}$ (M= Si or Zr), as is observed for these chemical species in the bulk phase. Therefore, the redox potential of the couple Co(III)/Co(II) is less affected for the electroactive species adsorbed on the SilZrP matrix. Since Co(III) is encapsulated in the cage formed by the ligand, the electronic density on the metal is affected by the contact ion-pair and hydrogen bonding between the anion of the supporting electrolyte and Co(sep). The shifts in mid-point potentials are affected by the nature and concentration of the anion.

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