IMMOBILIZATION OF ETHYLENESULFIDE ON SILICA SURFACE USING ACID AND BASE CATALYSTS
Adsorption and thermodynamic data

Luiza N. H. Arakaki[1]*, Maria G. da Fonseca[1], J. G. P. Espínola[1], A. F. Wanderley[1], E. P. S. Martins[1], T. Arakaki[2] and C. Airoldi[3]

[1]Departamento de Química-CCEN, Universidade Federal da Paraíba, 58.051-900, João Pessoa, Paraíba, Brazil
[2]Departamento de Tecnologia Química e Alimentos-CT, Universidade Federal da Paraíba, 58.051-900, João Pessoa, Paraíba, Brazil
[3]Instituto de Química, Universidade Estadual de Campinas, 13083-970 Campinas, São Paulo, Brazil

The reaction of cyclic ethylene sulfide with 3-aminopropyltrimethoxysilane resulted in a new silylating agent, which was anchored onto a silica surface via the sol-gel procedure using hydrochloric acid or ammonium hydroxide as acid or base catalysts, respectively. Both organofunctionalized surfaces have the ability to adsorb divalent cations from aqueous nitrate solution. Through calorimetric titrations, the thermodynamic data of cation-basic center interactions were obtained. Exothermic enthalpy values were obtained for all interaction processes. The calculated free Gibbs energy is in agreement with the spontaneity of the reactions and the positive entropy values for all reactions are favorable for these systems.

Keywords: acidic and basic catalysis, calorimetric titration, ethylenesulfide, hybrid sol–gel process silicas, tetraethoxysilane, thermodynamic data

Introduction

Since the second half of the previous century the study of surface proprieties of inorganic solids, mainly in porous materials has been growing considerably. Much research effort has been devoted to study the physicochemical modification on the support of these materials especially to be endowed with specific proprieties. The interest in organofunctionalized materials is because these materials exhibit wide technological applicability, such as catalysis or support for catalyst [1, 2], high performance liquid chromatography [3], cation removal [4–7], ion exchanger [8], adsorption for organic compounds [9], as well as a medium for attaching biologically active components used in sensors [10], and for other applications. There are several procedures to modify a supporter. The conventional immobilization methods using pure activated silica gel require relatively high temperature (higher than 373 K) for several hours. The sol-gel method as a normal procedure to synthesize many kinds of porous silicas is based on the hydrolysis of tetraethoxysilane (TEOS). Depending on the purpose of the application of the final material the preparation conditions can be changed to adjust the desired reaction. Besides, the sol-gel method has several advantages compared to that one utilized in the normal coating procedure [11, 12]. The advantage

of the sol–gel technique for the immobilizing molecule is the fact that the reaction can be carried out at room temperature enabling the introduction of organic molecules into an inorganic matrix without deteriorating their functionalities [13]. In the sol–gel process, the reactions are much more rapid and the degree of functionalization of the material can be controlled [11].

The purpose of the present study was to verify the influence of acid or base catalysis on the structure of the anchored material synthesized by using the sol–gel process from the hydrolysis of TEOS and 2-{2-{3-(tri-methoxysly)propylamino}ethylthio} ethanethiol in aqueous medium. The modified matrix synthesized by base catalysis (BC) was previously investigated in an attempt to explore the capacity for adsorbing transitions metal cations in aqueous solutions [13]. Synthesis of new material using acid catalysis (AC) and the adsorption capacity of divalent cobalt, nickel and copper from aqueous solution was not yet reported in the literature, which justifies such determinations in the present work. Beside this, the new material showed a high capacity in adsorbing these series of cations when compared to other adsorbents [4, 6, 14, 15]. Other interesting aspect is related to the stability of the solid. The use of high pH, BC, could affect the structure of siloxane groups. Consequently, the matrix synthesized using BC presented low surface area; this

* Author for correspondence: luiza_arakaki@yahoo.com.br

means that the support has small pores and small density, which interferes in adsorption capacity because some solids are in suspension in aqueous solutions. On the other hand, the case with matrix synthesized by AC presented a major stability in aqueous solutions in view of the use of low pH, which does not affect the siloxane structure of the silica. The surface area is three times higher than BC matrix. Thus, the support has a major quantity of pores in which water could penetrate causing sedimentation of the material. As a consequence the profile of adsorption isotherms and calorimetric titrations measurements are in accordance which was expected without any oscillations and getting very adjustable figures. Another purpose in the development of this research is to work in aqueous solutions around pH=6.7.

Experimental

Materials

Ethylenesulfide, etc, (Aldrich) was distilled before use. Tetraethoxysilane, TEOS, (Aldrich) and 3-(trimethoxysilyl)propylamine, APTS, (Aldrich) were used without previous purification. Hydrated divalent copper (Carlo Erba), nickel (Carlo Erba) and cobalt (Vetec) nitrates were also used without purification and the concentration was determined through complexometric titration with standard EDTA solution. All other chemicals have a reagent grade.

Synthesis of 2-{2-{3-(trimethoxysilyl)propyl-amino}ethylthio}ethanethiol (NSSH)

The new silylant agent was synthesized in an anhydrous condition by mixing 20.0 cm^3 (57.28 mmol) of the precursor 3-(trimethoxysilyl)propylamine (APTS) with 7.0 cm^3 (114.56 mmol) of ethylenesulfide, maintained in a slight reflux in sand bath at 373 K in a sealed tube for 24 h to give the final product of reaction NSSH.

Immobilization of silylant agent NSSH onto silica gel

All silicas were obtained by hydrolysis of the precursor alkoxides employing mineral acid (HCl) or base (NH$_4$OH) as catalysts. First, TEOS and NSSH were mixed with ethanol in a 2:1 molar ratio, being the last reagent responsible for the immobilization of the organic molecule in the hybrid polymer. This final reactant mixture reached a 1:4:1 molar ratio of alkoxides, water and ethanol, respectively. In base catalyst (BC) an amount of 3.0 cm^3 of ammonium hydroxide $8.0 \cdot 10^{-2}$ mol dm^{-3} was added drop wise to the result solution under stirring at 333 K. In acid catalyst (AC) 5 cm^3 of concentrated acid was slowly

added to the alkoxide solution under stirring in ice bath. Exothermic reaction took place with both catalysts and the gels were immediately formed, which were aged for 48 h at *r.t.* The white solid was filtered, washed with water, ethanol and then dried up under vacuum at *r.t.* for 8 h.

Methods

The surface of the silicas was characterized by the determination of surface area through BET method [16] by using Flowsorb II 2300 Micrometrics apparatus.

Mass loss determination was performed on a DuPont thermogravimetric instrument, Model 951, using 5–15 mg of sample under argon atmosphere, with a programmed heating rate of 0.17 K s^{-1}. The nitrogen content of the silicas obtained by acid or basic catalysis was determined by the Kjeldahl method, and the elements analyzed through a PerkinElmer 2400 Series II micro elemental analyzer instrument. These values reflect the degree of organofunctionalization on both kinds of matrices. ^{13}C and ^{29}Si nuclear magnetic resonance spectra for solid samples were obtained on an AC/300P Bruker spectrometer with cross polarization and magic angle spinning at a frequency of 75.47 MHz with acquisition time of 0.311 s, pulse repetition time of 4 s, contact time 1 ms and the number of scans were 20480 for ^{13}C and 59.62 MHz with acquisition time 0.110 s pulse repetition time at 4 s contact time 1 ms and the number of scans were 1303 for ^{29}Si.

Adsorption isotherms

The adsorption isotherms were obtained through batch method suspending 50 mg of modified silica samples in 20.0 cm^3 of aqueous solutions containing one of the cations at several different concentrations mechanically stirred for 2 h at 298 ± 1 K and separated by centrifugation for 10 min. Aliquots of the supernatant were pipetted and the cations were determined by the conventional EDTA complexometric titration using the appropriate indicator [17] for each metal. The adsorption capacity (mmol g^{-1}) was calculated by following the expression $n_f=(n_i-n_s)m$, where n_f is the number of moles adsorbed on the silica surface, n_i and n_s are the number of moles of the initial solutions and of the supernatant after the equilibrium, and m the mass of modified silica.

Calorimetry

The thermal effect evolved from the reaction was measured in an LKB 2277 calorimeter [13,15]. A sample of functionalized silica, varying from 15.0

to 50.0 mg, was suspended in 2.0 cm^3 of water in a steel ampoule under stirring at 298.15±0.02 K. Thermostated solutions of the cations in the $3 \cdot 10^{-3}$ to 0.10 mol dm^{-3} range were incrementally added into the calorimetric vessel [18]. The corresponding thermal effect of dilution of the cation solution was obtained in the absence of the silica (Q_d). The thermal effect of the hydration of the immobilized silica in water was evaluated as before [14]. The net thermal effect of adsorption (ΣQ_r) was obtained as in Eq. (1).

$$\Sigma Q_r = \Sigma Q_t - \Sigma Q_d \qquad (1)$$

Results and discussion

The reaction of the precursor silylating agent 3-(tri-methoxysilyl) propylamine with a double stoichiometric amount of ethylenesulfide under homogeneous conditions caused the opening of the three membered ring to yield the new silylating agent nominated NSSH, as described previously [11].

During the sol–gel process the copolymerization of TEOS with NSSH molecule occurs. The TEOS reagent starts the formation of the silica backbone through hydrolysis and NSSH is continuously incorporated onto the silicon matrix. A new material is formed in this process which combines the stability of the inorganic matrix associated to the chemical properties of the organic molecule [7, 11, 14].

When base catalyst (BC) is used, the anchored surface yielded 2.50 mmol g^{-1} of molecules covalently bonded per one gram of silica. This value contrasts to that one obtained with the acid catalysis (AC), which gave 0.85 mmol g^{-1} of pendant groups per gram of silica, calculated from elemental analysis. In an attempt to compare the structure of the organic chain attached to the inorganic backbone, obtained through sol-gel process the first feature examined was the carbon-13 solid-state NMR spectra shown in Figs 1 and 2. The profiles of those spectra are quite different presenting differences both in chemical displacements and in peak intensities. The profiles of these NMR spectra suggest two different organofunctionalized matrices.

The peaks related to the bonded immobilized silylating agent, obtained from AC, in Fig. 1 showed the methoxy carbon groups at 50.8 ppm and those attributed to carbons 1, 7 and 2 at 9.5, 16.4 and 19.9 ppm, respectively. The equivalent carbons 5 and 6 presented a peak at 32.0 ppm and finally the peak at 58.0 ppm is related to equivalents carbons 3 and 4. This observed sequence of signals is not the same to that obtained for a BC matrix. The large peak around 55 to 52 ppm is attributed to equivalent carbon 3 and 4, whose proposed structure and the
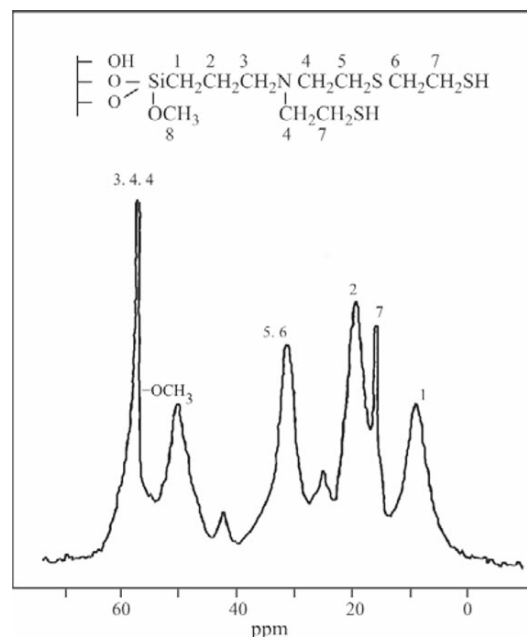

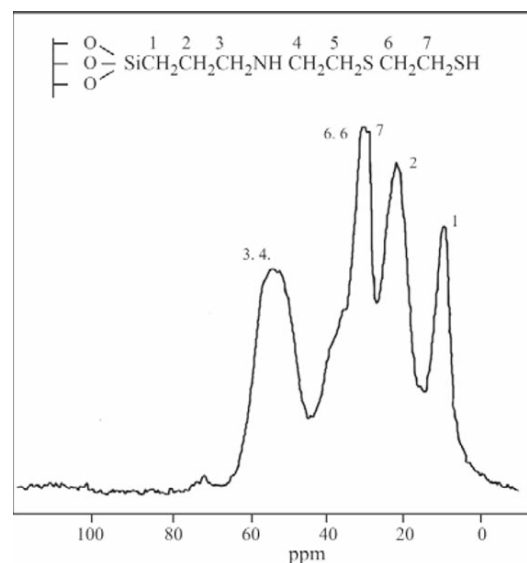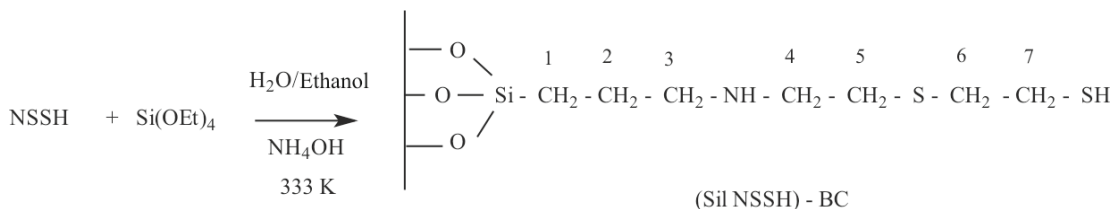**Fig. 1** ^{13}C CP/MAS NMR spectrum of silica synthesized through acid catalysis

Fig. 2 ^{13}C CP/MAS NMR spectrum of silica synthesized through basic catalysis

number of each carbons are indicated on the top of the right side of Fig. 2.

Then, the series of peaks were attributed as: at 33.1 ppm to carbon 6 and 5 at 23.8 ppm to carbons 2 and 7 and at 11.3 ppm to carbon 1 [11]. The ^{29}Si CP-MAS NMR spectrum for BC matrix presented a peak at −67.3 ppm followed by another two peaks. The peak at −109.9 ppm can be attributed to the presence of silicon atoms bonded to four siloxane groups, as represented by (Si(OSi≡)$_4$. The other one at −101.5 ppm indicated the existence

NSSH + Si(OEt)₄ →[H₂O/Ethanol] [NH₄OH] [333 K]

Scheme with structure:

— O\
— O — Si - CH₂ - CH₂ - CH₂ - NH - CH₂ - CH₂ - S - CH₂ - CH₂ - SH
— O/

(positions 1 2 3 4 5 6 7)

(Sil NSSH) - BC

Scheme 1

of an isolated silanol group where the silicon atom is bonded to a silanol groups and three other siloxane groups, such as represented by $(OH)Si(OSi\equiv)_3$ [10]. The intense peak at –67.3 ppm is attributed to silicon atoms bonded to three siloxane groups and one pendant organic chain [10], as represented by the reaction in Scheme 1.

The first difference observed from ^{13}C solid-state NMR spectrum is related to the presence of methoxy carbon groups on matrix synthesized by AC. The use of concentrated acid as catalyst could modify the structure of the silylating agent perhaps performing a rearrangement of the compound such as represented by the Scheme 2 of reaction.
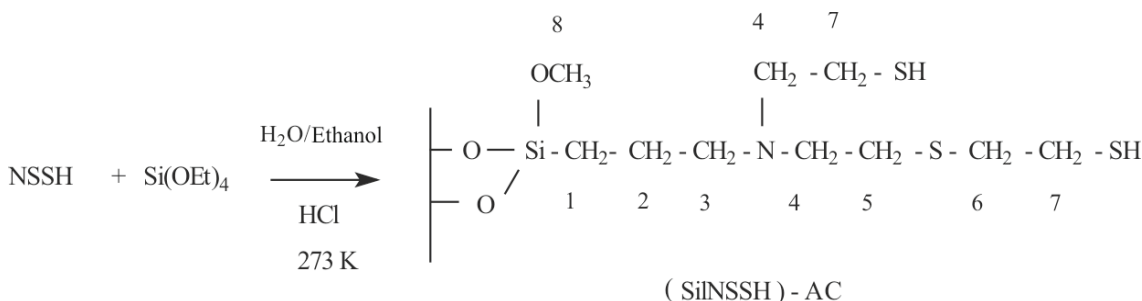
The TG curve of the immobilized silica SilNSSH – AC compound showed an initial 3.3% mass loss occurred in the 319 to 385 K temperature range, which is attributed to the evaporation of physically adsorbed water on the silica surface. The second mass loss of 13.1% happened in the 502 to 604 K range, which is related to the decomposition of organic groups covalently bonded on silica surface. The last mass loss of 4.5% occurred in the range 754 to 1124 K due to the condensation of silanol groups, yielding siloxane residue.

On the surface of SilNSSH – BC the TG curve showed a total mass loss of 51% without any definite steps, which could correspond to the decomposition of the organic groups with the condensation of remaining silanol groups to yield the final residue of siloxane.

The results of these two TG curves are in agreement with the elemental analysis of the compounds.

The surface areas of these materials were determined through the BET equation and the results obtained were 80±6 and 236±1 m² g⁻¹ for base and acid catalysis, respectively. These lower surface areas are due to the presence of pendant groups which block the access of molecules of gaseous nitrogen into the structure of the anchored silica [4, 5].

On examining the character of these materials the types of catalyst influence the structures of the silicas. Both silicas presented different ^{13}C spectra, TG curve, and surface areas indicating that both of them have different distribution of pendant groups on the surfaces with different chemical structures. These modified surfaces containing several basic centers composed by nitrogen and sulfur donor atoms are potentially available as chelating moieties to complex cations such as copper, nickel and cobalt from aqueous solutions [4, 5, 12]. The results of the adsorption of these cations on modified surfaces are presented in Table 1. The adsorption isotherms showed very similar profiles but vary on the capacity of adsorbing these cations from aqueous solutions. These variations in adsorption are related to the quantity of the basic centers that can be potentially used for coordinating metallic cations. However, as mentioned earlier the amounts anchored onto silica surface were 2.50 and 0.85 mmol from the BC and AC surfaces, respectively, despite the fact that the matrix synthesized by BC had anchored more than double and its adsorption capacity was less than AC matrix. This fact could be related to the easier diffusion of metallic cations with basic centers on AC surface in view of the small amount 0.85 mmol g⁻¹, of pendant groups on the surface. Uses of BC and AC

Scheme 2 structure:

NSSH + Si(OEt)₄ →[H₂O/Ethanol] [HCl] [273 K]

(position 8) OCH₃   (positions 4, 7) CH₂ - CH₂ - SH
               | |
— O — Si - CH₂- CH₂ - CH₂ - N - CH₂ - CH₂ - S - CH₂ - CH₂ - SH
— O/   1   2   3   4   5   6   7

(SilNSSH) - AC

Scheme 2

Table 1 Number of moles adsorbed (n_f), correlation coefficient (r) and metal basic center relationship (M/B) for each adsorption on SilNSSH matrix, with acid catalyst (AC) and base catalyst (BC)

SilNSSH	M^{2+}	n_f/mmol g^{-1}	r	M/B
	Cu	1.57±0.01	0.9952	2:1
AC	Ni	1.48±0.02	0.9959	1.7:1
	Co	1.23±0.04	0.9976	1.5:1
	Cu	1.46±0.01	0.9983	1:1.17
BC	Ni	1.11±0.10	0.9911	1:2.3
	Co	1.17±0.02	0.9995	1:2

Fig. 3 Calorimetric titration of SilNSSH-AC surface with cobalt nitrate at 298.15±0.02 K. The points in the experimental curve are the sums of the thermal effects: ■ – ΣQ_{tit}, ○ – ΣQ_{dil} and △ – ΣQ_{res}

have an influence on adsorption capacity as discussed at the end of the introduction section. Another evidence that the structure of siloxane groups is affected in BC matrix is related to the decomposition of the organic material in the TG curve. The first mass loss in modified silicas is always related to the elimination of physisorbed water, which in BC material does not occur. Adsorption measurements are difficult to perform due to the high pH and changes on the structure of siloxane group probably forming some ammonium silicate which results in a very fine material.
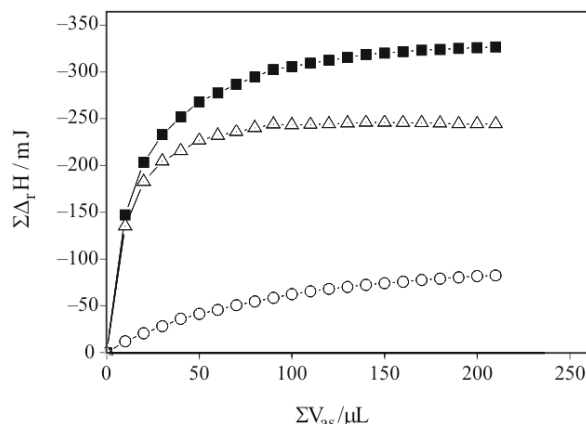
The metal-basic centers ratio were more than one metal grafting on each pendant group on AC matrix, while for BC surface there was one metal for two pendant groups, as shown in Table 1.

The thermodynamic data of the interactions of the divalent cations with the organofunctionalized surfaces were obtained by calorimetric titration through thermal effect measurements. As the thermal effect of the hydration of the support is null, the resultant value for the considered reaction was calculated by considering Eq. (1), whose corresponding values are shown in Fig. 3, as an example involving the calorimetric titration of cobalt.

The obtained results were adjusted to a modified Langmuir equation, Eq. (2), to calculate the integral enthalpy for formation of a monolayer per unit mass of adsorbent $\Delta_{mon}H$:

$$\frac{\Sigma X}{\Sigma \Delta_r H} = \frac{1}{(k-1)\Delta_{mon}H} + \frac{\Sigma X}{\Delta_{mon}H} \qquad (2)$$

where ΣX is the sum of the mole fractions of the cation in solution after each volume of titrand injected, X is obtained for each point of the titration from the batch experiments; $\Delta_r H$ is the integral enthalpy of adsorption (J g^{-1}) obtained by dividing the thermal effect of adsorption (Q_r) by the number of moles of the adsorbate; k is a constant of proportionality that also includes the equilibrium constant and $\Delta_{mon}H$ is the thermal effect of formation of the metal ion complex in a monolayer on the surface. $\Delta_{mon}H$ and k values were obtained from the slope and intercept of the $\Sigma X/\Delta_r H$ vs. ΣX plot. The resulting calorimetric isotherm and the respective linearized form for copper nitrate was adjusted to the above Langmuir modified equation as shown in Fig. 4. From these values, ΔG and ΔS values were calculated and the values are listed in Table 2.

From the equilibrium constant based on the $\Delta G = -RT\ln k$ expression the Gibbs free energy was calculated, whose negative values are in agreement with

Table 2 Thermodynamic data for the interaction of divalent cations (M^{2+}) on SilNSSH surfaces modified with acid catalyst (AC) and base catalyst (BC), at 298.15±0.02 K, and correlation coefficient (r)
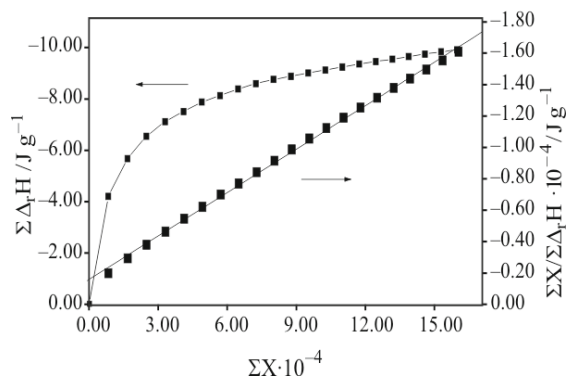
SilNSSH	M^{2+}	$-\Delta H$/kJ mol^{-1}	$-\Delta G$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}	r
AC	Cu	5.07±0.09	21.51±0.02	55±1	0.9993
	Ni	1.25±0.10	22.18±0.16	70±1	0.9997
	Co	4.47±0.39	25.11±0.31	69±1	0.9996
BC	Cu	7.40±0.01	25.80±0.10	62±1	0.9989
	Ni	1.50±0.10	35.10±0.15	42±1	0.9999
	Co	0.98±0.02	30.82±0.12	100±1	0.9998

Fig. 4 Isotherm of calorimetric titration of SilNSSH – AC surface with copper nitrate at 298.15±0.02 K. The straight line is a linearized form of the isotherm

the spontaneity of the reaction. The entropy values were calculated through the $\Delta G=\Delta H–T\Delta S$ expression and a series of positive values were also obtained. Such values are associated to the displacement of the hydrogen of water molecules bonded to the basic centers in addition to those identically bonded to cations to enrich the free solvent molecules as the reaction is in progress at the solid/liquid interface [15]. These thermodynamic data for each value found, reflect the sum of the results of more than one type of interaction which occurs between the cation and basic centers of the immobilized groups on the supports as formerly shown in relation to molar ratio of the metal/basic centers. For this reason it was not possible to establish a relationship between the enthalpy values for each adsorption process and the respective numbers of moles adsorbed per gram of the surfaces in the maximum coverage state.

These thermodynamic data showed that the anchored silicas form stable complexes with these divalent cations. The cation-basic center interactions with chelating atoms on pendant groups gave exothermic enthalpy values for divalent copper, nickel and cobalt, in both surfaces. The negative and positive values found for Gibbs free energy and entropy, respectively, are in agreement that the reactions are favorable for all systems studied. From the point of view of the entropy, both the water bonded to the nitrogen or sulfur basic centers and the hydrated cations affect these interactions of the metallic cations with the chelating groups causing an entropic enhancement. The transfer of water molecules from the hydration sphere to the medium of the reaction promotes the disorganization of the system and consequently leads to an increase in the entropy in all adsorption reactions [18] with predominance of cobalt due to its larger volume of hydration.

Conclusions

The present study showed that the type of catalyst employed in the sol–gel process affects the degree of immobilization and structure of the obtained materials. When concentrated acid and ice bath are used during the procedure of the reactions less pendant groups are yielded on the surface. On the other hand, more than double the amount of pendant groups anchored on silica surface is yielded when diluted basic solution is used and the temperature is kept to around 333 K. The final surfaces presented different adsorption capacities, being more favorable for AC matrix. The matrix synthesized by acid catalysis presented a major stability in water, which was observed in adsorption batch process and calorimetric measurements, as discussed in the introduction and results sections. A similar behavior between these two surfaces was demonstrated when thermodynamic data such as enthalpy, entropy and Gibbs free energy values were obtained for both surfaces. Excellent coefficient correlation values of each linearization were obtained for all systems. This fact implies that the data obtained with these surfaces showed a good adjustment to the Langmuir adsorption model. In these processes the interactive effects at these solid/liquid interfaces are in agreement with the formation of a cation monolayer on the surfaces of the modified silicas.

Acknowledgements

References

1 K. Suzuki, Y. Aoyagi, N. Katada, M. Choi, R. Ryoo and M. Niwa, Catal. Today, 132 (2008) 38.

2 A. Naydenov, P. Konova, Pen. Nikolov, F. Klingstedt, N. Kumar, D. Kovacheva, P. Stefanov, R. Stoyanova and D. Mehandjiev, Catal. Today, 137 (2008) 471.

3 H. Zhong, G. Zhu, P. Wang, J. Liu, J. Yang and Q. Yang, J. Chromatogr. A, 1190 (2008) 232.

4 V. L. S. Augusto Filha, O. G. Silva, J. R. Costa, A. F. Wanderley, M. G. Fonseca and L. N. H. Arakaki, J. Therm. Anal. Cal., 87 (2007) 621.

5 K. S. Sousa, V. L. S. Augusto Filha, V. H. A. Pinto, M. G. Fonseca, J. G. P. Espínola and L. N. H. Arakaki, Quim. Nova, 30 (2007) 528.

6 L. N. H. Arakaki, M. G. Fonseca, E. C. Silva Filho, A. P. M. Alves, K. S. Sousa and A. L. P. Silva, Thermochim. Acta, 450 (2006) 12.

7 E. Ispir and S. Serin, J. Therm. Anal. Cal., 94 (2008) 281.

8 C. Airoldi, Quim. Nova, 31 (2008) 144.

9 S. Štandeker, Z. Novak and Z. Knez, J. Colloid Interface Sci., 310 (2007) 362.

10 O. Nadzhafova, M. Etienne and A. Walcarius, Electrochem. Commun., 9 (2007) 1189.

11 C. R. Silva and C. Airoldi, J. Colloid Interface Sci., 195 (1997) 381.

12 V. Musat, P. Budrugeac and C. Gheorghies, J. Therm. Anal. Cal., 94 (2008) 373.

13 C. Airoldi and L. N. H. Arakaki, Polyhedron, 20 (2001) 929.

14 C. Airoldi and L. N. H. Arakaki, J. Colloid Interface Sci., 249 (2002)1.

15 L. N. H. Arakaki, A. P. M. Alves, E. C. Silva Filho, M. G. Fonseca, S. F. Oliveira, J. G. P. Espinola and C. Airoldi, Thermochim. Acta, 453 (2007) 72.

16 S. Brunauer, P. Emett and E. Teller, J. Am. Chem. Soc., 60 (1938) 309.

17 H. A. Flaschka, EDTA Titration, An Introduction to Theory and Practice, 2nd Ed., Pergamon Press, Oxford 1967.

18 J. A. A. Sales, A. G. S. Prado and C. Airoldi, Surf. Sci., 590 (2005) 51.