

The Li⁺, Na⁺ and K⁺ ion exchange reaction process on the surface of mixed oxide SiO₂/TiO₂/Sb₂O₅ surface prepared by the Sol-Gel processing method

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Abstract: The porous mixed oxide SiO₂/TiO₂/Sb₂O₅ obtained by the sol-gel processing method presented a good ion exchange property and a high exchange capacity towards the Li⁺, Na⁺ and K⁺ ions. In the H⁺/M⁺ ion exchange process, the H⁺ / Na⁺ could be described as presenting an ideal character. The ion exchange equilibria of Li⁺ and K⁺ were quantitatively described with the help of the model of fixed tetradentate centers. The results of simulation evidence that for the H⁺ / Li⁺ exchange the usual situation takes place: the affinity of the material to the Li⁺ ions is decreased with increasing the degree of ion exchange. On the contrary, for K⁺ the effects of positive cooperativity, that facilitate the H⁺ / K⁺ exchange, were revealed.

Keywords: silica-titania-antimonia mixed oxide; ion exchange; alkaline metal ions; stability constants.

Introduction

The synthetic inorganic ion exchangers include an important class of materials because they are normally obtained as rigid matrices and do not swell in aqueous solutions, normally presenting good chemical selectivity associated with a high thermal and chemical stabilities [1,2].

Among these materials, titanium (IV) antimonate has been described as a good ion exchanger [3-6]. It has been prepared by mixing aqueous solutions of Ti (IV) and SbCl₅ and the precipitated solids separated by filtration. However, this method has not been lead to a useful product because fine powders and samples having low specific surface areas were normally obtained [7-11]. Alternatively, the sol-gel processing method has been used to prepare materials with characteristics of high homogeneity and purity, controlled porosity and well-modeled particles [12-14]. The material prepared by using this procedure,

presented also high ion exchange capacities towards the alkaline metal ions in the following order of increasing affinity: Li⁺<Na⁺<K⁺ [15]. In order to explain the mechanism of the exchange process and in particular the higher affinity of the material by the heavier metal ion along the serie, the process of H⁺/M⁺ exchange on the sorbent surface should be studied in more detail. The model of an ideal exchange process as normally used to calculate the equilibrium constants in solids such as organic resins apparently can not to be applied to porous solid presenting a heterogeneous surface. A model that takes into consideration the lateral interaction on the solid surface between the neighbor acid sites which can affect the exchange process must be considered [16,17]. The aim of this work is to describe and discuss the ion exchange process of Li⁺, Na⁺ and K⁺ ion on the surface of porous SiO₂/TiO₂/Sb₂O₅ material using the polidentate fixed acid centers model. This model was used to describe and to estimate the stepwise equilibria constants.

Experimental part

The $\text{SiO}_2/\text{TiO}_2$ mixed oxide was prepared according to procedure described elsewhere [15]. The $\text{SiO}_2/\text{TiO}_2$ binary oxide was prepared in three steps according to the procedures described as follows: (1) 12.1 ml of 0.85 mol l⁻¹ HNO_3 aqueous solution was added to 250 mL of 50% (v/v) tetraethoxysilane (TEOS)/ethanol solution, and the mixture was stirred at 353 K for 2.5 h. (2) About 21 ml of titanium (IV) butoxyde (TBO) and 490 ml of ethanol were then added and the mixture was stirred for 2 h at room temperature. (3) 66 ml of 0.6 mol l⁻¹ HNO_3 solution were slowly added and allowed to rest for gelation. The formed xerogels were ground, dried at 383 K for 24 h and sieved in order to obtain particles size between 75 and 250 μm .

Incorporation of Sb(V) into $\text{SiO}_2/\text{TiO}_2$

About 15 g of the mixed oxide obtained was immersed in 500 ml of distilled water and 20 ml of 0.3 mol l⁻¹ Sb (V) (prepared from SbCl_5) aqueous solution were added and the suspension heated at 333 K for 8 h. The solid was filtered, washed with 1.0 mol l⁻¹ HNO_3 solution in order to avoid Sb(V)

hidrolysis and to eliminate choride ion, and finally with deionized water until the washing solution achieved a neutral pH.

Ion exchange isotherms

The ion exchange capacities for the sample was determined by weighing about 100 mg of the materials and adding into 50.0 mL of 1.0 mol l⁻¹ MCl solution ($M = \text{Li}^+, \text{Na}^+, \text{K}^+$) and shaken for 8 h at 298 K. 25.0 mL of the supernatant solution was titrated with standard 0.05 mol l⁻¹ NaOH solution [2]. The isotherms were determined by immersing 100 mg of $\text{SiO}_2/\text{TiO}_2/\text{Sb}_2\text{O}_5$ into 50 ml of the ions with concentrations between 8×10^{-5} and 5×10^{-3} mol l⁻¹. Each mixture was shaken about 24 h at 298 K and the concentration of the metal ion in the solution phase was determined. The measurements were carried out on a B 262 Micronal flame photometer apparatus.

Results and discussions

The main characteristics of the solid obtained, SiO_2TiO_2 and $\text{SiO}_2/\text{TiO}_2/\text{Sb}_2\text{O}_5$ are summarized in Table 1. For sake of brevity, both solids will hereafter designated as ST and STSb.

Table 1. Chemical analyses results, surface areas and average pole volumes for $\text{SiO}_2/\text{TiO}_2$ and $\text{SiO}_2/\text{TiO}_2/\text{Sb}_2\text{O}_5$

Samples	Ti /wt %	Sb /wt %	S_{BET} /m ² g ⁻¹	V_p /ml g ⁻¹
$\text{SiO}_2/\text{TiO}_2$	11.6	-	607	0.52
$\text{SiO}_2/\text{TiO}_2/\text{Sb}_2\text{O}_5$	10.2	9.8	528	0.44

Table 1 shows that the Sb content is 9.8 wt% which corresponds to 0.8 mmol g⁻¹ of the element in the matrix. The specific surface areas determined by the BET method, shows an area of 528 m²g⁻¹ for STSb and 607 m²g⁻¹ for ST. The results show that for STSb the blocking of the finest pores by the antimony oxide is not significant and thus, the decrease of the area upon coating the ST surface is very small.

Ion exchange isotherms

Figures 1a-c show the ion exchange

isotherms for Li^+ , Na^+ and K^+ ion on STSb at 298 K. Clearly we observe that at the limit of saturation condition on the isotherm curves the adsorption capacities are $\text{Li}^+ < \text{Na}^+ \sim \text{K}^+$. The ion exchange process on the solid surface can be represented by the equation:



where the bars mean the solid phase and

K_{exch} is the concentration equilibrium constant,

$$K_{\text{exch}} = \frac{[\text{H}^+][\overline{\text{M}}^+]}{[\overline{\text{H}}^+][\text{M}^+]} \quad \text{eq 2}$$

where the concentrations in solution phase are expressed as mol l⁻¹ and in the solid phase as mol g⁻¹.

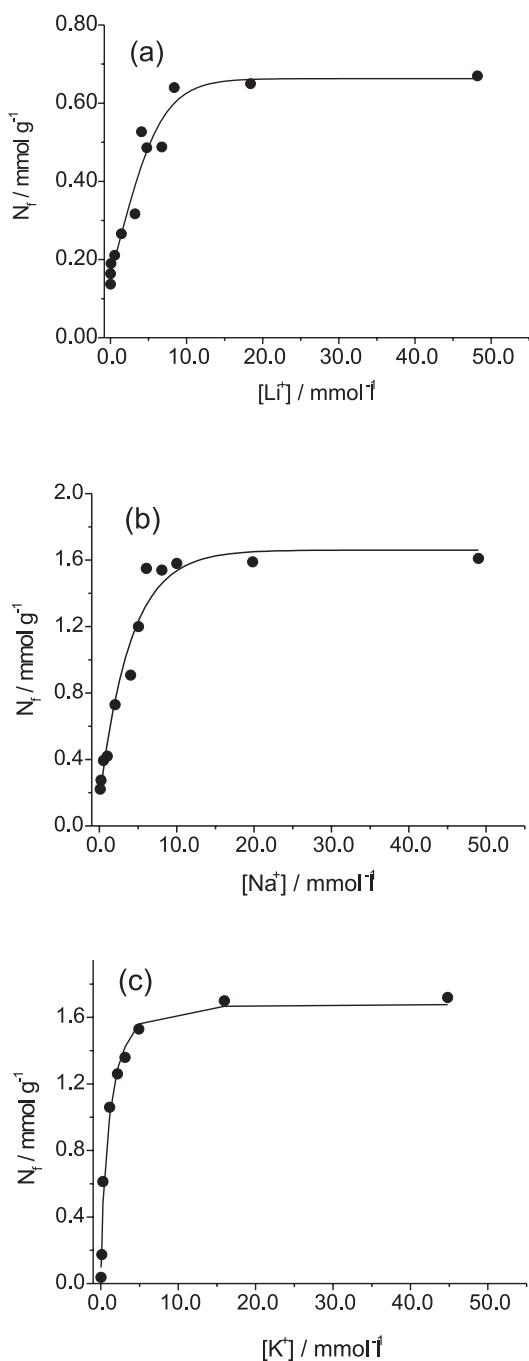


Figure 1. Ion exchange isotherms at 298K on STSb for (a) Li⁺, (b) Na⁺ and (c) K⁺

Simulations of ions-exchange equilibria

The initial values of $\log K_{exch}$ were estimated for all experimental points with the use of eq 2, for different molar fraction of the metal, $\overline{\chi}_M$, on the solid phase STSb. For an ideal ion exchange case is expected $\log K_{exch}$ value do not depend on $\overline{\chi}_M$. As an example, Figure 2 shows the plot of $\log K_{exch}$ plotted against $\overline{\chi}_{K^+}$.

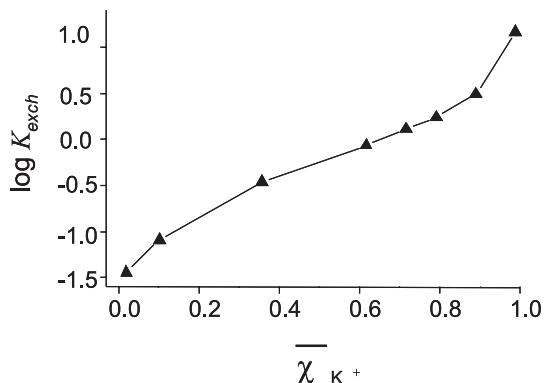
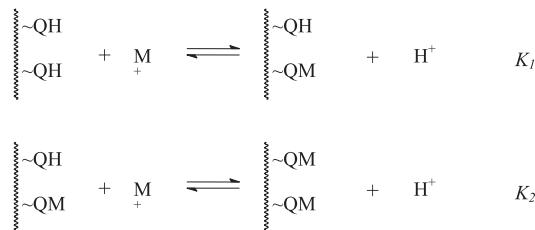


Figure 2. Plot of $\log K_{exch}$ against $\overline{\chi}_{K^+}$ for an ion exchange process on STSb at 298 K.

We observe that the ion exchange process H⁺/K⁺ do not correspond to the model of the ideal exchange, *i.e.* the replacement of H⁺ with K⁺ leads to increasing of $\log K_{exch}$. The deviation from an ideal model is also observed for the exchange process H⁺/Li⁺ and H⁺/Na⁺. These results are indicating that the energetical heterogeneity of the materials manifest at the H⁺/M⁺ exchange process. Both, the quantitative description of the ion exchange equilibria and characteristics of the material require taking this feature into account. There are several possible ways to perform this [18-23]. In this work the model of fixed polydentate centers has been used [16,17]. According to it, the surface of the material is considered as the assemblage of the polydentate ion exchange centers whereas the ion exchange process is represented by the scheme below, where the stepwise equilibrium

reactions are characterized with the corresponding constants $K_1, K_2, K_3\dots$

Scheme 1. Ion exchange as presented by the model of the fixed bidentate centers. $\sim\text{QH}$ is the center of the ion exchange.



The overall constants are defined as

$\beta_i = K_1 \times K_2 \times K_3 \times \dots = \prod_{i=1}^Z K_i$, where Z is the number of the stages. To use the model it is necessary to determine the size of the center (Z) and to calculate the values of K_i or β_i .

The following procedure was used to solve this task.

Step 1. The tentative value $Z=1$ was fixed.

Step 2. The unknown concentration equilibrium constants b_i were calculated by the nonlinear least-square method [24] applied to minimize criterion

$$\chi^2_{\text{exp}} = \sum_{k=1}^N w_k \Delta_k^2 \quad \text{eq 3}$$

where k is the number of the experimental

points, Δ_k is the difference between the calculated and experimental values, $\Delta = C^{\text{calc}} - C^{\text{exp}}$ or $\Delta = N_f^{\text{calc}} - N_f^{\text{exp}}$, where C is the equilibrium concentration of the metal ions in solution (mol l^{-1}), N_f is the specific amount of the adsorbed metal ions (mol g^{-1}), w_k is the statistical weight of the K^{th} measurement assigned as:

$$w_k = \frac{1}{A_k^2 \cdot \sigma_r^2} \quad \text{eq 4}$$

where A_k is the experimental value (C or N_f) and σ_r is its relative error [25]. All computations were performed with the aid of the software program CLINP 2.1 [26].

Step 3. The adequacy of the model was tested. If the model fitted experimental data unsatisfactorily, the current Z value is increased and new calculations of the equilibrium constants are performed (see step 2).

To test the adequacy of the models, the global criterion χ^2 is used [27]. The model is assumed to be adequate if the following inequality holds,

$$\chi^2_{\text{exp}} < \chi^2_f(5\%) \quad , \quad \text{eq 5}$$

where $\chi^2_f(5\%)$ is the 5% point of the chi-squared distribution with f degrees of freedom ($f = N - x$, where x is the number of the parameters to be calculated).

It was found that the acceptable quality of fitting the experimental data is attained at $Z = 4$ (model of fixed tetradentate centers). Figure 3 presents the example of simulation for the H^+ / K^+ exchange. The course of simulation and the results of calculations are summarized in Tables 2-4.

Table 2. The results of testing the model of the ideal ion exchange for the H^+ / Na^+ exchange*

	The fit of C	The fit of N_f
$\chi^2 / \chi^2_f(5\%)$	9 / 16.9	
Assigned values of – $\sigma_r(C)$ – $\sigma_r(N_f)$	0.05 –	– 0.10
$\log K_{\text{exch}}$	-0.20 (0.03)	-0.18 (0.03)
χ^2_{exp}	15.4	16.1

*Here and below the values in parentheses are the standard deviations.

Table 3. The results of simulation of the H⁺ / Li⁺ exchange

	The fit of C	The fit of N _f
Assigned values of - σ _r (C) - σ _r (N _f)	0.03 —	— 0.10
Model of the ideal ion exchange (Z = 1)		
Log K _{exch}	-0.27 (0.05)	0.9 (0.8)
F / χ _f ² (5%)		11 / 19.7
χ _{exp} ²	95.5	268
Model of fixed bidentate centers (Z = 2)		
Log β ₁	0.21 (0.04)	0 (0.6)
log β ₂	-1.6 (0.7)	0.1 (0.4)
F / χ _f ² (5%)		10 / 18.3
χ _{exp} ²	39.6	69.3
Model of fixed tridentate centers (Z = 3)		
Log β ₁	0.63 (0.02)	0.55 (0.25)
log β ₂	redundant parameter*	redundant parameter*
log β ₃	-1.21 (0.14)	-1.28 (0.24)
F / χ _f ² (5%)		10 / 18.3
χ _{exp} ²	7.2	21.4
Accepted model of fixed terdentate centers (Z = 4)		
Log β ₁	0.95 (0.06)	1.2 (0.4)
log β ₂	0.23 (0.03)	-0.2 (0.8)
log β ₃	redundant parameter*	redundant parameter*
log β ₄	-1.31 (0.20)	-1.0 (0.4)
F / χ _f ² (5%)		9 / 16.9
χ _{exp} ²	6.2	10.1
Average weighted estimates:		
log β ₁		0.96 (0.06)
log β ₂		0.22 (0.03)
log β ₄		-1.25 (0.18)

* It is impossible to calculate the equilibrium constant because at all experimental points the degrees of formation of the reaction product do not exceed 0.01% of the total Li⁺ concentration.

Table 4. The results of simulation of the H⁺ / K⁺ exchange

	The fit of C	The fit of N _f
Assigned values of – σ _r (C) – σ _r (N _f)	0.03 –	– 0.10
Model of the ideal ion exchange (Z = 1)		
Log K _{exch}	-1.12 (0.23)	-0.43 (0.23)
F / χ _f ² (5%)		8 / 15.5
χ _{exp} ²	524	91.4
Model of fixed bidentate centers (Z = 2)		
Log β ₁ log β ₂	Redundant parameter -0.98 (0.14)	redundant parameter -0.63 (0.17)
F / χ _f ² (5%)		8 / 15.5
χ _{exp} ²	118	24.9
Model of fixed tridentate centers (Z = 3)		
Log β ₁ log β ₂ log β ₃	Redundant parameter redundant parameter -0.94 (0.10)	redundant parameter redundant parameter -0.81 (0.14)
F / χ _f ² (5%)		8 / 15.5
χ _{exp} ²	32.2	16.9
Accepted model of fixed teradentate centers (Z = 4)		
Log β ₁ log β ₂ log β ₃ log β ₄	Redundant parameter -1.3 (0.3) redundant parameter -1.08 (0.15)	redundant parameter -1.3 (0.6) redundant parameter -1.02 (0.12)
F / χ _f ² (5%)		7 / 14.1
χ _{exp} ²	12.0	4.55
Average weighted estimates:		
log β ₂ log β ₄		-1.30 (0.25) -1.25 (0.19)

One important feature of the H⁺ / K⁺ ion exchange should be noted. When the replacement of H⁺ by K⁺ in the tetradeinate center $\overline{\text{H}_4\text{Q}_4}$ occurs, it is impossible to determine the stepwise ion exchange constants K_i . That is for the reason that the intermediate species $\overline{\text{KH}_3\text{Q}_4}$ and $\overline{\text{K}_3\text{HQ}_4}$ are practically absent. This fact points to the non-

stepwise character of the ion exchange process. In other words, if H⁺ in the tetradeinate center is replaced by K⁺, the replacement of the next H⁺ ion is facilitated, the K⁺ ion “pushes out” the next hydrogen ion. As a rule, such positive cooperativity is rarely happened. But it seems that such situation is not the exceptional case for the hybrid materials

on the base of inorganic oxides. A similar example of the positive cooperativity for such materials was recently described [28]. Unfortunately, the scarcity of information about this new generation of materials does not allow to propose now more or less clear explanation of the revealed phenomenon and requires further investigation.

Degrees of formation of different species

in the solid phase (Figures 4 and 5) corroborate a great difference between the nature of the ion exchange process for Li^+ and K^+ . In the case of the H^+ / Li^+ exchange, species $\overline{\text{LiH}_3\text{Q}_4}$, relatively depleted with Li^+ , predominates at extents of reaction 0.15 – 0.55, while for the H^+ / K^+ ion exchange species, enriched with K^+ , is the main potassium entity in the solid phase

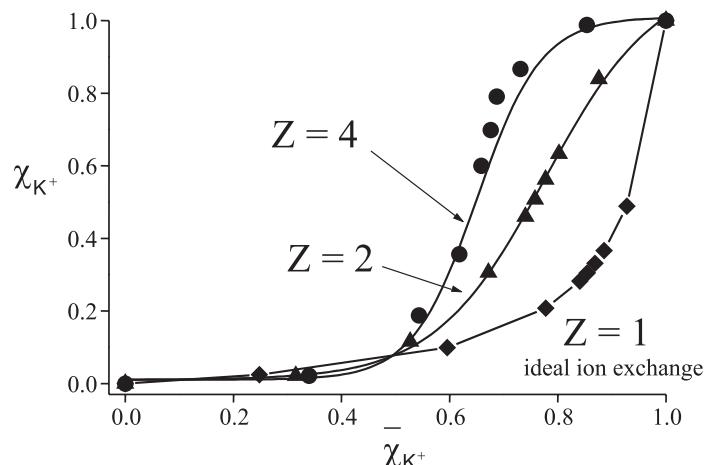


Figure 3. The ion exchange isotherm of K^+ . χ_{K^+} is the molar fraction of K^+ in aqueous solution and χ_{K^+} is the molar fraction of K^+ in solid phase.

Conclusions

The porous solid STSb showed a good ion exchange property possessing a high exchange capacity towards the Li^+ , Na^+ and K^+ ions.

In the H^+/M^+ ion exchange process, the H^+ / Na^+ could be described as presenting an ideal character. The ion exchange equilibria of Li^+ and K^+ were quantitatively described with the help of the model of fixed tetradeятate centers. The results of simulation evidence that for the H^+ / Li^+ exchange the usual situation takes place: the affinity of the

material to the Li^+ ions is decreased with increasing the degree of ion exchange. On the contrary, for K^+ the effects of positive cooperativity, that facilitate the H^+ / K^+ exchange, were revealed.

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Resumo: O óxido misto poroso SiO₂/TiO₂/Sb₂O₅, obtido pelo método de processamento sol-gel, apresentou uma boa propriedade e elevada capacidade de troca iônica com os íons Li⁺, Na⁺ e K⁺. No processo de troca iônica H⁺/M⁺, o H⁺/Na⁺ apresentou um caráter ideal. Os equilíbrios de troca de Li⁺ e K⁺ foram quantitativamente descritos através de um modelo de centros tetracentrados fixos. Os resultados de simulação evidenciaram que para troca H⁺/Li⁺ temos uma situação normal: a afinidade do material pelo íon Li⁺ decresce com o aumento do grau de troca. Para o K⁺, o efeito positivo do cooperativismo que facilitaria a troca H⁺/K⁺, revelou um efeito contrário.

Palavras-chave: óxido misto de silica-titania-antimonia; troca iônica; ions de metais alcalinos; constantes de estabilidade.

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