INVESTIGATION ON THE FACTORS INFLUENCING THE MECHANISM OF THE ALKALINE SORPTION ON THE SURFACE OF TITANIUM PHOSPHATE SORBENT*

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Abstract

Studies were made on clarifying of the sorption mechanism on the surface of amorphous titanium phosphate inorganic sorbent determining the "dissolving" values, specific surface area and pore distribution. The pore distribution has changed under the effect of the eluent. The selectivity observed for this type of the titanium phosphate is not connected with the macroscopic surface structure and geometry but rather with the geometry of the active sites.

Introduction

Recently in research and industry (e.g. semiconductor industry, production of high-purity materials and catalysts etc.) there are an increasing number of fields where the adequate qualification of surfaces, i.e. the composition and structure of the surface, is important.

In the last two decades the number of the more and more sophisticated and precise methods (e.g. SEM, LEED, RHEED etc.) has grown rapidly. Some of these have become applied routinely in specific fields, but due their cost and complexity they have not been applied widely in chemical laboratories. That is also why it is worth recommending the use of conventional methods. In many cases the combined use of several such methods can yield sufficient information cost effectively.

Furthermore the materials investigated, because of their chemical properties, can damage sophisticated high value surface testing instruments; if this is so, we must also revert to conventional methods.

Both these arguments played a role in our decision to investigate the influence of the surface structure on the sorption mechanism of amorphous titanium phosphate with specific sorption properties prepared in very strong acidic media with conventional physical and physico-chemical methods. We wish to present a part of this range of experiments to illustrate the

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* Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

above-mentioned points. A method was elaborated in our laboratory for preparing an amorphous titanium phosphate inorganic sorbent with specific sorption properties for alkaline ions [1, 2, 3]. The results of our different investigations indicated that under those experimental circumstances the sorption processes on this titanium phosphate were not or not only ion exchange processes. This preparation in contradiction to similar materials written about in the literature does not bind the whole range of alkaline ions, but only those of them which are characterized by a crystalline ionic radius greater than 0.13 nm, i.e. lithium and sodium is hardly or not at all sorbed. The separation factor for the other alkaline ions is in the order of 10^3—10^4, that for most analytical and preparative purposes makes satisfactory separation possible.

Both because the specific sorption properties of this kind of titanium phosphate differs from those described in the literature, and also because of the desirability of clarifying further application possibilities, it was necessary to determine the sorption mechanism, which is probably closely related to the surface structure.

Experimental

The sorbents tested were prepared using the method described elsewhere [1]. For the experiments sorbents with significantly different qualities were used. (They were: TPA 150 with "poor" sorption properties ($F_{\overset{\approx}{\text{sep}}}\, 10^2$) and the "good" TPA 153 with an $F_{\overset{\approx}{\text{sep}}}\, 10^3$.)

Testing of sorption quality was carried out with the method described earlier [1]. The only difference was that instead of using ^{42}K radiotracer the concentration of inactive potassium was measured by flame photometry. The instrument was a Flamom type flame photometer. The flame was produced by using propane-butane gas and air.

The solubility tests were done in two ways: in static system and dynamically. The static experiments were done by Ward's method [4]. In spite of the fact that Ward's method is suitable for the determination of "solubility" the differentiation of the "real" and colloidal solutions is not possible; in order to call attention to this fact instead of the "solubility" the expression "dissolving" is used.

The dynamic "dissolving" tests were done both with distilled water and 6 mol/l hydrochloric acid using the elution column method to model the same technique used to qualify the sorbents. The specific surface area was calculated using a sorptometer developed at the Department for Physical Chemistry TU Budapest [5].

The pore distribution measurements were carried out by using a CARLO-ERBA M 70H type high pressure mercury porosimeter.

Results

The "dissolving" in distilled water under static circumstances in the case of the sample TPA 153 was twice as much as with TPA 150 (Table 1).

The dynamic "dissolving" in distilled water with TPA 153 was also greater than with the other sorbent. The dynamic "dissolving" in 6 mol/l hydrochloric acid with TPA 153 was again almost twice as much as with TPA 150.

Table 1

Results of "dissolving" tests

Sorbent code	Static "dissolving" in distilled water [g/100 cm^3]	Dynamic "dissolving" in distilled water [g/100 cm^3]	Dynamic "dissolving" in 6 m HCl [g/100 cm^3]
TPA 150	0.10	0.35	0.51
TPA 153	0.20	0.43	0.92

Table 2

Specific surface areas before and after elution

Sorbent code	Before elution [m^2/g]	After elution with distilled water [m^2/g]	After elution with 6m HCl [m^2/g]
TPA 150	1.57	1.39	0.79
TPA 153	105.25	56.81	25.68

Comparing the specific surface areas (Table 2) we can conclude that the specific surface area of the TPA 153 sorbent is one order of magnitude greater than that of the TPA 150. Also the eluent used influences the result; in both cases there is a decrease in the specific surface area, but this decrease is greater with the acid than with distilled water. With both eluents the one order magnitude difference between TPA 153 and TPA 150 remained. These results show a good correlation with the values obtained during determination of the "dissolving".

The pore distribution curves can be seen in figures 1 and 2. The TPA 153 sample had pores of two discernible radii ranges 10^2—10^3 nm and 4—7 nm. (The average pore radius of the pores with smaller diameters and the specific pore volume belonging to this were determined as the abscissa and

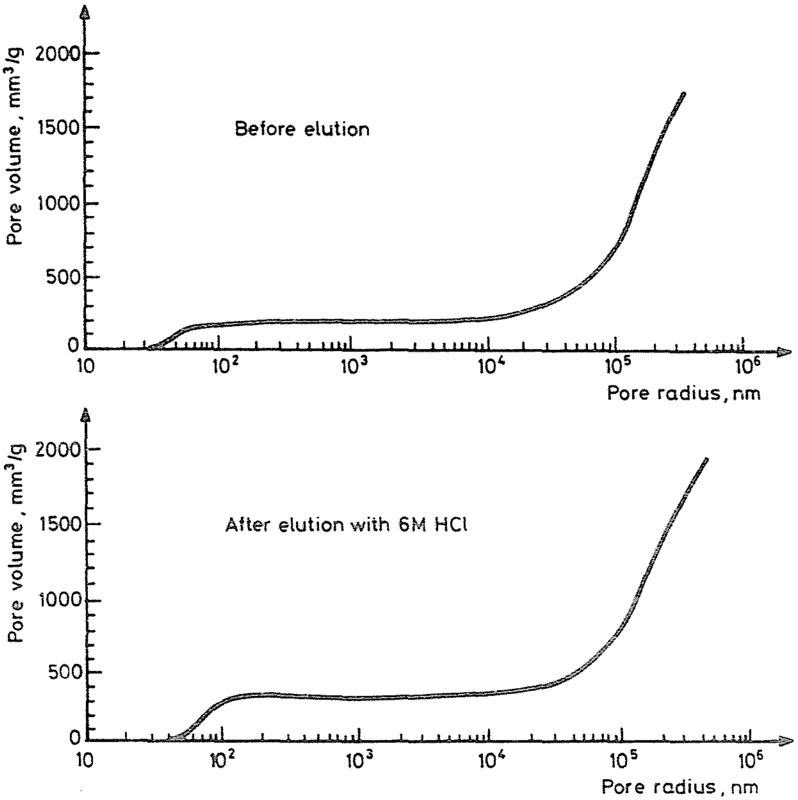

Fig. 1. Pore distribution curves of the TPA 153 sorbent

the ordinate of the inflexion points of the step to be found in this range. The values obtained such a way were 5 nm and 70 mm^3/g respectively.) The total pore volume of the larger pores was less than that of the smaller ones.

The pore distribution of the TPA 153 material loaded by K^+ ions in 6 mol/l hydrochloric acid became changed (Fig. 1). The average pore radius and the specific pore volume belonging to this sample increased (pore radius: 6.2 nm, specific pore volume: 170 mm^3/g) and the specific surface area decreased at the same time (Table 2). This probably indicates that a part of the "walls" separating the pores have burst because of "dissolving" so the pore volume and the pore radius increased, but at the same time the internal surface of the particle decreased.

The TPA 150 sorbent practically did not contain any pores of small diameter; the characteristic pore size of this sample was in fact in a broad range between 10 and 10^4 nm (Fig. 2). The specific surface areas of the TPA 150 materials changed similarly to those of the TPA 153 under the effect of the elution i.e. under the effect of the eluent (solvent!) (Table 2). The explanation

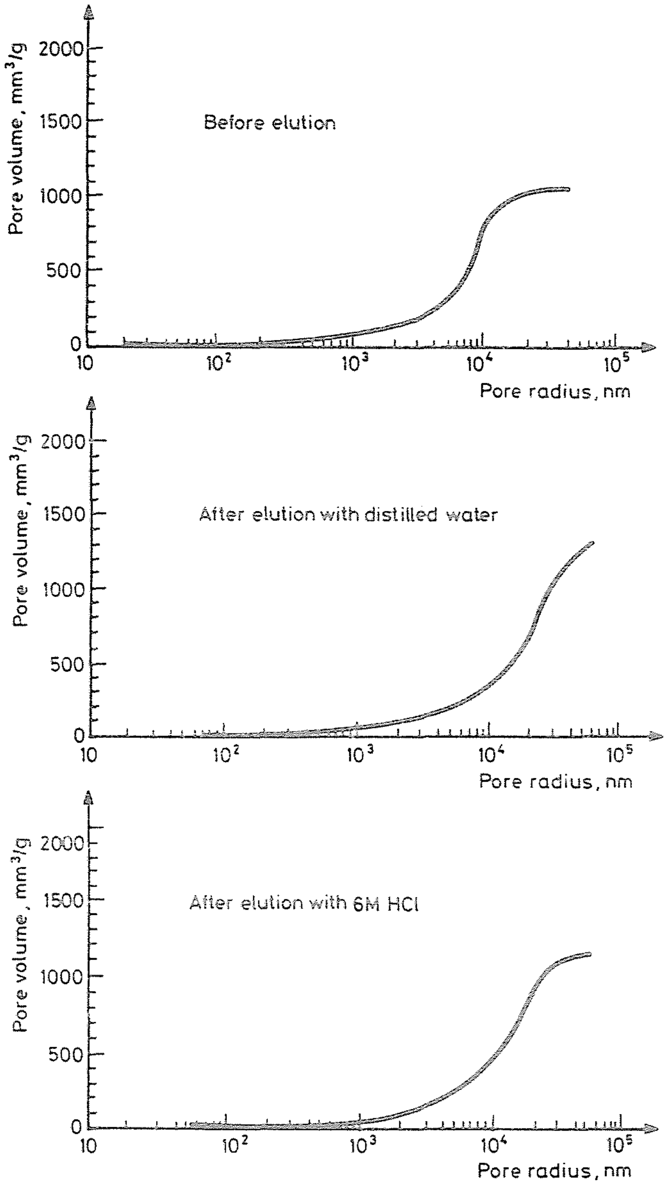

Fig. 2. Pore distribution curves of the TPA 150 sorbent

of this phenomenon was presumably similar to that mentioned above concerning the TPA 153 sorbent.

On the basis of our previous investigations [3] it seems to be probable that within the complex sorption processes the active sites responsible for the sorption of different ions differ from each other.

Through the present experiments a view was obtained of the structure of the sorbent and it can be stated that the selectivity observed for ions of crystalline ionic radius greater than 0.13 nm is not connected with the macroscopic surface structure and geometry but rather with the geometry of active sites (energetical inhomogenities). These are not directly connected to the pore size, for the pore sizes of the amorphous product are greater by about one order of magnitude than the sizes of the ions, hydrated ions and ion-pairs existing in the liquid phase [6].

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