

# Hydrous oxides of titanium: cation exchange properties and kinetics of exchange

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The ion exchange properties of hydrous titania gels of different particle sizes, precipitated from titanous chloride through the agency of ammonium carbonate and hydroxide have been studied. Such studies were carried out under acidic and alkaline conditions with respect to  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions.

In the case of gels precipitated by ammonium carbonate, oxygen gas was used as the oxidizing agent whereas with ammonium hydroxide as precipitant, oxidation was performed with hydrogen peroxide.

Ion exchange capacities were determined by visible spectrophotometry. Increasing the pH of preparation lead to an increase in exchange capacities of the hydroxide precipitated gels that are characterized to be mesoporous. Such an increase is not observed in the case of carbonate precipitated microporous gels. It is shown that in the latter case the  $\text{NH}_4^+$  ions generated by the initial interaction of  $(\text{NH}_4)_2\text{CO}_3$  with the acidic titanous chloride lead to the formation of titania exchangers that are predominantly in the ammonium form. The textural characteristics of the exchanger resulting from different conditions of preparation is a significant contributing parameter to the resulting data.

Ageing of the microporous titania samples markedly reduces the exchanger capacity of the smaller  $\text{Ni}^{2+}$  ions but increases that of the bulkier  $\text{Cr}^{3+}$  as a result of the presence of some wide pores that appear upon agglomeration. The presence of  $\text{Cr}^{3+}$  ions in the hydroxo form in solution seems to inhibit its exchange with the appropriate surface species.

Studies on the kinetics of exchange with respect to the  $\text{Ni}^{2+}$  ions seem to indicate that a particle diffusion mechanism is partly or completely responsible for the rate of exchange.

## 1. Introduction

The great number of investigations carried out during the last decade on hydrous titania, ranging from molecular sieve studies to the determination of ion exchange selectivity and kinetics of exchange, emphasize the industrial importance of  $\text{TiO}_2 \cdot x\text{H}_2\text{O}$  as a cation exchanger with a wide scope of applications.

Studies undertaken by a number of workers [1–8] have shown that hydrous titania has ion exchange characteristics that are highly dependent on the preparation conditions. Some of these investigations have also indicated that there existed different hydroxyl groups on the titania surface and that these were responsible for the cation exchange (and sometimes anion exchange) properties displayed by these gels. Others [9–12] have demonstrated the amphoteric nature of the titania surface.

A systematic study of the ion exchange properties of titania gels prepared from titanous chloride using, respectively, ammonium carbonate and hydroxide as precipitating agents in conjunction with oxygen gas and hydrogen peroxide as oxidizing agents, has not as

yet been reported. It is, therefore, the aim of this work to study the ion exchange properties of titania gels prepared by these methods in an attempt to correlate these properties with both the conditions of preparation of the gels and their resulting porosities.

## 2. Experimental procedure

### 2.1. Materials

Two series of titania gels  $T_C$  and  $T_H$  were prepared from titanous chloride using ammonium carbonate and ammonium hydroxide, respectively, as precipitating agents.

In the  $T_C$  series of gels, a saturated solution of  $(\text{NH}_4)_2\text{CO}_3$  was added to a 20%  $\text{TiCl}_3$  solution until the required pH was obtained – 8.0 and 4.7. The total volume was diluted with distilled water and oxygen gas bubbled through it until the dark coloured hydrous titania changed to the white titanic form. Each of gels  $T_{C8}$  and  $T_{C5}$  (pH 8.0 and 4.7, respectively) was then immersed for several days in distilled water, with frequent stirring, followed by washing until free

from chloride ions then dried in air for 10 days at  $25(\pm 0.5)^{\circ}\text{C}$ .

In the case of the  $T_H$  series, oxidation was achieved by adding excess  $\text{H}_2\text{O}_2$  (30 volumes) to a 20%  $\text{TiCl}_3$  solution. This was followed by the addition of 1:2 ammonia solution until the required pH was reached. Oxidation and precipitation occurred simultaneously. When oxidation was complete, the gel was filtered, washed till free from chloride ions and dried in air for 10 days at  $25(\pm 0.5)^{\circ}\text{C}$  giving gels  $T_{H8}$  and  $T_{H5}$  (pH 8.5 and 5.0, respectively).

Samples from both series were dried in air at  $110^{\circ}\text{C}$  for 24 h giving rise to samples  $T'_{C8}$ ,  $T'_{C5}$ ,  $T'_{H8}$  and  $T'_{H5}$ .

Textural characterization of the  $T_C$  series of samples has shown [13] them to be essentially microporous and that the preparation obtained at the lower pH possessed both a slightly smaller specific area (apparent) and a smaller total pore volume than that prepared at the higher pH. Titania gels prepared by the use of ammonia solution for their precipitation, as in the case with the  $T_H$  series, were also previously characterized to be composed of mesopores that widen with increase in pH [14].

All gels were ground in an agate mortar and sieve sized into  $(-60 + 100)$  ( $r = 0.01$  cm) and  $(-100 + 200)$  ( $r = 0.005(5)$  cm) fractions.

Both series of samples  $T_C$  and  $T_H$  were amorphous to X-rays.

Part of gels  $T_{C8}$  and  $T'_{C8}$  was converted to the hydrogen form through immersion in 0.2 M HCl.

## 2.2. Methods

The "equilibrium" ion exchange capacities or uptake (according to the isoelectric point) of the hydrous oxide was equilibrated for 48 h with 10 ml of 0.01 M solution of the desired cations at  $30(\pm 0.5)^{\circ}\text{C}$  - these are  $\text{Co}^{2+}$  (pH = 5.8),  $\text{Ni}^{2+}$  (pH = 6.3),  $\text{Cu}^{2+}$  (pH = 4.6) and  $\text{Cr}^{3+}$  (pH = 3.3). The exchanger was separated from solution and the liquid phase was analysed spectrophotometrically by Beer's method. The cations lost from solution are assumed to be adsorbed by the accurately weighed titania sample of known  $\text{TiO}_2$  content. Determinations were carried out in duplicate and good reproducibility was obtained.

Ion exchange kinetics were determined by equilibrating 0.6 g of the appropriate exchanger with 30 ml of the desired cation of known concentration. The solution was kept at  $27(\pm 0.5)^{\circ}\text{C}$  by using a thermostat and continuously stirred. 3 ml aliquots were withdrawn at different time intervals and their equilibrium concentration and "equilibrium" ion exchange capacity determined.

Infrared studies were carried out using a 1430 Perkin-Elmer ratio recording spectrophotometer. Solid samples were prepared in the form of a KBr pellet. 2 mg of the compound were mixed with approximately 200 mg of KBr (spectroscopic grade) and then subjected to a pressure of about 20 lb in $^{-2}$  (1 lb in $^2 = 6.894 \times 10^3$  Pa) in a hydraulic press. A disc of pure KBr was used in the reference cell.

A UV 5240 Beckmann ratio recording spectrophotometer was used to measure the absorbances in

the visible region of the electromagnetic spectrum using optically clean quartz cells.

## 3. Results

### 3.1. Infrared studies

Infrared results obtained on gels  $T'_{C8}$ ,  $T_{C8}$ ,  $T'_{C5}$  and  $T_{C5}$  are reported in Fig. 1 (curves a to d). Bands at 1000 and 1110  $\text{cm}^{-1}$  belong to the bending modes of hydroxo complexes, the 1000  $\text{cm}^{-1}$  being related to the bending mode of a "bridging" OH and the 1110  $\text{cm}^{-1}$  to a bending mode of a terminal OH [15, 16]. The 1400 and 1440  $\text{cm}^{-1}$  bands are characteristic of ammonium ions presumably originating from the ammonium carbonate (precipitating agent), trapped in different sites within the lattice [17]. The 1630  $\text{cm}^{-1}$  band is related to the bending mode of molecular water. The lower intensities of the 1400 and 1440  $\text{cm}^{-1}$  bands in the case of gels  $T'_{C8}$  and  $T'_{C5}$  are noteworthy. Heat treatment at  $\sim 110^{\circ}\text{C}$  has probably led to the desorption of some  $\text{NH}_4^+$  ions in the form of  $\text{NH}_3$  gas.

The infrared spectra of gel  $T_{C5}$  after immersion in 0.01 N  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  solutions are also shown in Fig. 1 (curves e and f).

A close observation of these curves indicates that immersion of gel  $T_{C5}$  for 48 h in  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  has led to significant decrease of the strong 1400  $\text{cm}^{-1}$  band and the concomitant disappearance of the 1440  $\text{cm}^{-1}$  shoulder. The intensities of the bridging hydroxo bands remaining virtually unchanged. Comparable results were obtained with gel  $T_{C8}$ .

The spectrum obtained after immersion for 24 h of gels  $T_{C8}$  and  $T_{H5}$  in 0.2 N HCl are also shown in the same figure (curves g and h). It is seen that immersion has resulted in a very drastic decrease of the 1400  $\text{cm}^{-1}$  band indicating a replacement of the  $\text{NH}_4^+$  ions by  $\text{H}^+$  from HCl. A decrease in the intensity of the 1110  $\text{cm}^{-1}$  band is also noted and confirms the amphoterism of the  $\text{TiO}_2$  surface where basic terminal OH groups may react with HCl.

In an attempt to totally convert gel  $T'_{C8}$  to the ammonium form, it was immersed for 24 h in 0.2 N  $\text{NH}_4\text{OH}$ . The infrared spectrum of the ammonia immersed  $T'_{C8}$  gel indicated an increase in the 1400  $\text{cm}^{-1}$  band, relative to the "hydroxo bands" but did not lead to the total removal of the latter bands (Fig. 1 (curve i)). The striking similarity between the spectrum of this gel and that of  $T_{C8}$  and  $T_{C5}$  (curves b, d) is noteworthy.

Such observations coupled with others in the next section all seem to strongly indicate that gels  $T_{C5}$  and  $T_{C8}$  are predominantly in the ammonium form.

### 3.2. Cation uptake

Table I shows the cation uptake for the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  ions by both air-dried samples and those dried at  $\sim 110^{\circ}\text{C}$  from both  $T_C$  and  $T_H$  series. All values given relate to the same concentration of cations (0.01 M) and for identical ratios of sorbent to solution (0.1 g of sorbent to 10 ml of solution).

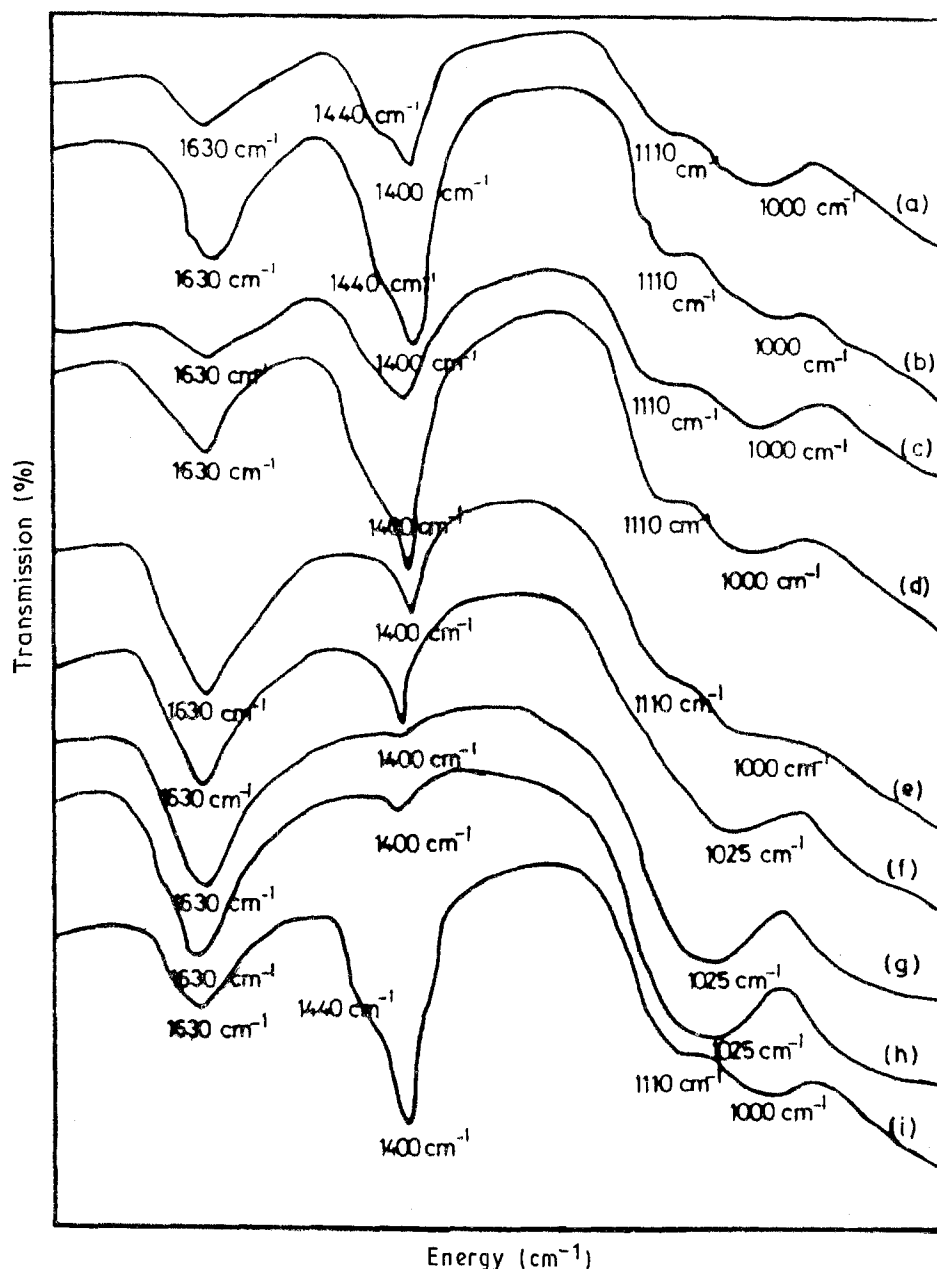


Figure 1 Comparative infrared spectra determined on gels  $T_{C8}$ ,  $T_{C8}$ ,  $T_{C5}$ ,  $T_{C5}$  (curves a, b, c, d); Infrared spectra of gel  $T_{C5}$  after immersion in 0.01 M  $Ni(NO_3)_2$  and 0.01 M  $Cr(NO_3)_3$  solutions (curves e, f); Infrared spectra of gels  $T_{C8}$  and  $T_{H5}$  after immersion in 0.2 N HCl (curves g, h) and Infrared spectrum of  $T_{C8}$  after immersion in 0.2 N  $NH_4OH$  (curve i).

In view of the fact that the isoelectric point of amorphous titania gels can be taken as around  $pH = 4.7$ , it is probable as shown elsewhere [18] that the uptake of the  $Cr^{3+}$  ( $pH = 3.3$ ) and  $Cu^{2+}$  ( $pH = 4.6$ ) occurs through an adsorption mechanism (possibly through complexation with the OHs on the surface) whereas in the case of  $Co^{2+}$ ,  $Ni^{2+}$  ( $pH = 5.8$  and  $6.3$ , respectively) an ion exchange mechanism is more plausible.

The wavelengths ( $\lambda$ ) at which the absorbance was measured are at 512, 397, 610, and 411 nm for  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Cr^{3+}$ , respectively. No changes were observed in these wavelengths upon using the various sorbents except in the case when  $Cr^{3+}$  was used with the titania that is dried at  $110^\circ C$  only. In this latter case a shift towards longer wavelengths was observed that reached 427 nm when  $Cr(NO_3)_3$  was used alone (i.e. in the absence of any electrolyte). Such a shift is

normally observed when one or more hydroxo groups replace the aquo group in the inner co-ordination sphere of the  $[Cr(H_2O)_6]^{3+}$  ions. In these experiments the pH was actually found to increase after the exchange equilibrium is attained, more markedly for samples from series  $T_C$  than from series  $T_H$ , pointing to an increase in the  $OH^-$  ions in solution. It appears that upon heating the titania gels to  $110^\circ C$  the solid loses the adsorbed water and also  $NH_3$  from trapped  $(NH_4)_2CO_3$  (see previous section) that probably had a "surface charge compensating" effect through excessive H-bonding. This heating process results in a bare surface with some unbalanced surface charges. The increase in  $OH^-$  ions in the solution may thus arise from several possible factors as (a) the anion exchange with the basic surface  $OH^-$  groups (that can also be used as adsorption sites for  $Cr^{3+}$ ) this, however, could not be detected by the bulk IR spectra used here,

TABLE I Cation exchange capacities of titania gels

Sample	pH of preparation	Capacity (meq g <sup>-1</sup> TiO <sub>2</sub> )					
		Co <sup>2+</sup> pH = 5.8	Ni <sup>2+</sup> pH = 6.3	Cu <sup>2+</sup> pH = 4.6	Cr <sup>3+</sup> pH = 3.2	Ni <sup>2+</sup> pH = 5.5	Cr <sup>3+</sup> pH = 3.4 in 1 M NaCl
Mesh size (- 100 + 200)							
T <sub>H5</sub>	5.0	1.28	1.22	1.40	1.80		
T' <sub>H5</sub>	5.0	1.22	1.00	1.26	1.50		
T <sub>H8</sub>	8.5	1.48	1.46	1.52	2.10		
T' <sub>H8</sub>	8.5	1.34	1.32	1.36	1.80		
T <sub>C5</sub>	4.7	1.15	1.16	1.56	2.34	0.89	2.05
T' <sub>C5</sub>	4.7	0.93	0.88	1.29	0.70	0.81	1.50
T <sub>C8</sub>	8.0	1.15	1.14	1.48	2.23	0.84	2.01
T' <sub>C8</sub>	8.0	1.14	1.00	1.31	-	0.72	0.54
Mesh size (- 60 + 100)							
T <sub>C5</sub>	4.7		1.24		-	0.86	1.86
T' <sub>C5</sub>	4.7		1.08		-	0.82	0.76
T <sub>C8</sub>	8.0		1.12		1.76	0.85	1.88
T' <sub>C8</sub>	8.0		1.00		-	0.66	-

(b) the selective uptake of H<sup>+</sup> from solution by the heated titania thereby displacing the water dissociation equilibrium. The presence of any polynuclear species [19] resulting from the hydrolysis of Cr<sup>3+</sup> is excluded since it would result in a decrease in pH. It is worth noting that in the preparation series T<sub>C</sub> any oxidation of trapped Ti<sup>3+</sup> [20] to Ti<sup>4+</sup> could not result in an increase in the pH of solution [21].

From Table I it can be seen that increasing the pH of precipitation has led, in the case of the T<sub>H</sub> series, to an obvious increase in the uptake of the cations and not a decrease as was observed for the uptake of Cr(vi) [22]. This might result from an increase in the acidic bridging hydroxyl ions on the surface, that, from a previous study [8] on a similar preparation with oxygen used as oxidant, were found to increase with increase in the pH of preparation. Moreover, pore widening was also found [14] to occur upon increasing the pH of precipitation thereby not only reducing possible diffusion effects during the exchange process but also exposing new surfaces thereby increasing the exchange capacity and cation uptake. This does not, however, seem to be the case for the air-dried T<sub>C</sub> series of gels where either identical or slightly lower values were obtained with an increase in the preparation pH. This series of samples is characterized [13] by being microporous with a slight increase in total pore volume as well as an increase in specific surface area (apparent) upon increase in pH of preparation. Such variations in surface characteristics normally result from the presence of a larger number of pores of probably narrower pore sizes than that obtained for samples prepared at lower pH. Accordingly the results obtained for the ion uptakes are believed to be quite reasonable, bearing in mind that stripping of the hydration water from the exchanging ions must occur during their entrance [23].

Table I also indicates that drying in air at ~ 110 °C results in the formation of titania gels with lower

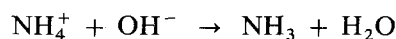
uptake capacities. Such results are in keeping with previously reported ones [8] where heat treatment at 110 °C was shown to lead to a partial collapse of the structure through the removal of interstitially bound water. Besides, after dehydration, the probability of exchange of basic OH<sup>-</sup> with NO<sub>3</sub><sup>-</sup> anions or adsorption of H<sup>+</sup> ions onto these sites increases after removing the film of adsorbed water thereby decreasing the uptake of the cations in the form of strongly adsorbed species. The greater decrease in uptake observed for the Cr<sup>3+</sup> cations may also result from the preferential uptake of the hydroxo species by these ions in solution [24] that appear to retard or even inhibit their exchange (or adsorption) with the corresponding surface species. In the case of the T<sub>C</sub> series of gels, the NH<sub>4</sub><sup>+</sup> ions also seem to play a crucial role in terms of exchange capacities so that heat treatment at 110 °C may also lead to their desorption in the form of NH<sub>3</sub> and hence contribute to the observed decrease in exchange capacities. Meanwhile one should not neglect the uptake of some water molecules from the solution by these heated samples which may result in a minimal variation in concentration especially if the cation exchange is small. From the above discussion and taking into consideration the larger size of Cr<sup>3+</sup> ions and their greater stability [24] in the hydroxo form over the other tested cations this explains the marked decrease in the uptake of Cr<sup>3+</sup> ions being almost nil for sample T'<sub>C8</sub>.

The presence of 1 M NaCl solution during the exchange experiments was tested with the T<sub>C</sub> series and using Ni<sup>2+</sup> and Cr<sup>3+</sup> ions and is found to have a decreasing effect on the cation exchange values obtained for the exchange of Ni<sup>2+</sup> by both the air-dried samples and those heated at 110 °C. This observation was also noticed in the case of Cr<sup>3+</sup> ions by the air-dried samples of smaller size only (*r* = 0.005(5) cm) whereas the reverse was true for almost the rest of the samples except sample T'<sub>C8</sub> of larger size that did not

exhibit any exchange. It appeared ambiguous that samples that almost exhibit no uptake for  $\text{Cr}^{3+}$  when water only was used as for example samples  $T_{C5}$  and  $T'_{C5}$  of particle size 0.01 cm, gave relatively appreciable values in presence of 1 M NaCl. The exact role of NaCl other than its effect on the stabilization of the ionic strength is not quite clear but it seems to be related to the inhibition of the process resulting in the increase in  $\text{OH}^-$  ions in solution. This is reflected in the values of  $\lambda$  that are found to decrease from 427 nm (in presence of water only) to 418 nm in presence of NaCl such an effect is also marked when HCl is used and will be discussed soon. It thus appears that the presence of the hydroxo group in the inner coordination sphere of  $\text{Cr}^{3+}$  ions hinders its exchange with the appropriate surface species.

The effect of ageing for three months was investigated for samples with mesh size (-60 +100) ( $r = 0.01$  cm) and for samples  $T_{C8}$  and  $T'_{C8}$  only. The cation exchange capacities for  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  on these samples are given in Table II before and after immersion in 0.2 N HCl for several days.

The exchange capacities for  $\text{Ni}^{2+}$  ions by these samples are found, after ageing, to be lower than those determined before ageing (Table I, column 4). Such results indicate a certain degree of ageing in these gels and are in keeping with the work of Inoue and Yamazaki [25] who showed that a  $\text{TiO}_2$  hydrate cation exchanger displayed an abrupt decrease in its cation exchange capacity three months after preparation. In the present work ageing may have led to the reaction of ammonium and hydroxyl ions on the surfaces, namely



leading to the elimination of some of the exchangeable ammonium ions (that form significant exchangeable sites) as well as some basic adsorption sites which are also significant in the cation uptake.

The uptake of  $\text{Cr}^{3+}$  ions are found to be higher for the aged gels that were not immersed in HCl (i.e. not converted to the hydrogen form) than those before ageing. It is worth noting that sample  $T'_{C8}$ , that previously exhibited no exchange, gave a value of 0.41 meq  $\text{g}^{-1}$  for the aged sample. This is contrary to what was observed for  $\text{Ni}^{2+}$  ions. Bearing in mind that these samples are, however, microporous the ageing process seems to have produced some agglomeration of the particles that result in some pore widening on the expense of the narrower pores. In such a

situation,  $\text{Ni}^{2+}$  of small ionic radius will be deprived of some sites that were located in the collapsed narrower pores whereas for  $\text{Cr}^{3+}$  of larger ionic radius, now have available wider pores that permit their uptake in sites that were previously inaccessible to these ions.

Soaking the samples in 0.2 N HCl for 48 h did not affect the cation exchange values of the  $\text{Ni}^{2+}$  ions whereas the uptake of  $\text{Cr}^{3+}$  has decreased markedly being then comparable to the values obtained by  $\text{Ni}^{2+}$  ions.

It is worth noting that the shift in  $\lambda$  from 411 nm in the  $\text{Cr}^{3+}$  determination has disappeared when 0.2 N HCl was used and has also decreased from 427 to 418 nm for the aged samples.

### 3.3. Kinetics of ion exchange

It has been reported that the ion exchange mechanism for adsorption of ions, from rapidly stirred concentrated solutions is controlled by the diffusion rates of adsorbed and desorbed ions within the ion exchange particle for both organic ion exchange resins and inorganic ion exchangers.

Boyd, Adamson and Myers [26] showed that if the ion exchange rate is controlled by particle diffusion, the fractional exchange  $F$ , at time  $t$ , by particles of spherical radius  $r$  is given by

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2} \quad (1)$$

where the rate constant is

$$B = \pi^2 D_i / r^2 \quad (2)$$

$D_i$  is the effective diffusion coefficient for the pair of ions being exchanged.

$F$  is a calculable mathematical function of  $Bt$ , and to check Equation 2, it is most convenient to obtain  $Bt$  for each value of  $F$  from the Reichenberg's tables of  $Bt$  and  $F$  [27] and to plot against the experimental time.

Provided  $D_i$  is independent of  $F$ , the result should be a straight line of slope  $B$  and passing through the origin. Good linear  $Bt$  against  $t$  plots are shown in Figs 2 and 3 for the  $T_C$  and  $T_H$  series of gels. These provide preliminary evidence that in the present system, particle diffusion is the rate controlling mechanism.

Equation 2 also predicts that the rate constant  $B$  for a given exchanger will decrease inversely with the square of the particle radius assuming the average

TABLE II Effect of immersing gels  $T_{C8}$  and  $T'_{C8}$  after ageing for three months for 48 h in 0.2 M HCl

Sample Mesh size [-60 +100]	$\text{Ni}^{2+}$	$\text{Cr}^{3+}$	$\lambda$ of supernatant liquid of $\text{Ni}^{2+}$	$\text{Cr}^{3+}$
48 h in 0.2 N HCl				
$T_{C8}$	0.24	0.18	397	411
$T'_{C8}$	0.28	0.24	397	411
Without 0.2 N HCl				
$T_{C8}$	0.20	0.41	397	418
$T'_{C8}$	0.28	1.68	397	418

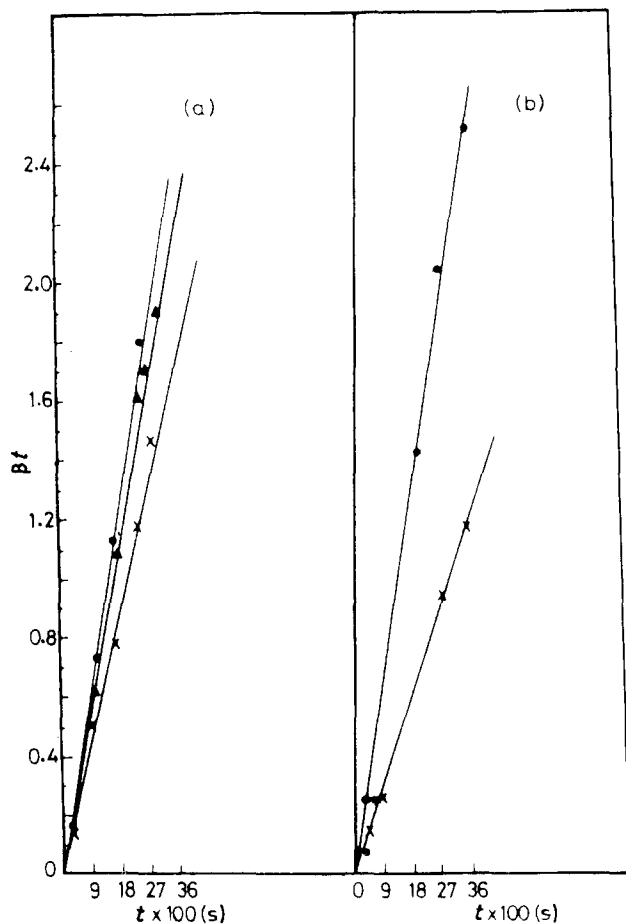


Figure 2  $Bt$  plotted against  $t$  (a) ●  $T_{C8}$  (-60 + 100) with 0.3 M  $Ni(NO_3)_2$ , ▲  $T_{C8}$  (-60 + 100) with 0.2 M  $Ni(NO_3)_2$ , ×  $T_{C8}$  (-100 + 200) with 0.2 M  $Ni(NO_3)_2$ ; (b) ●  $T_{C5}$  (-60 + 100) with 0.2 M  $Ni(NO_3)_2$ , ×  $T_{C5}$  (-100 + 200) with 0.2 M  $Ni(NO_3)_2$ .

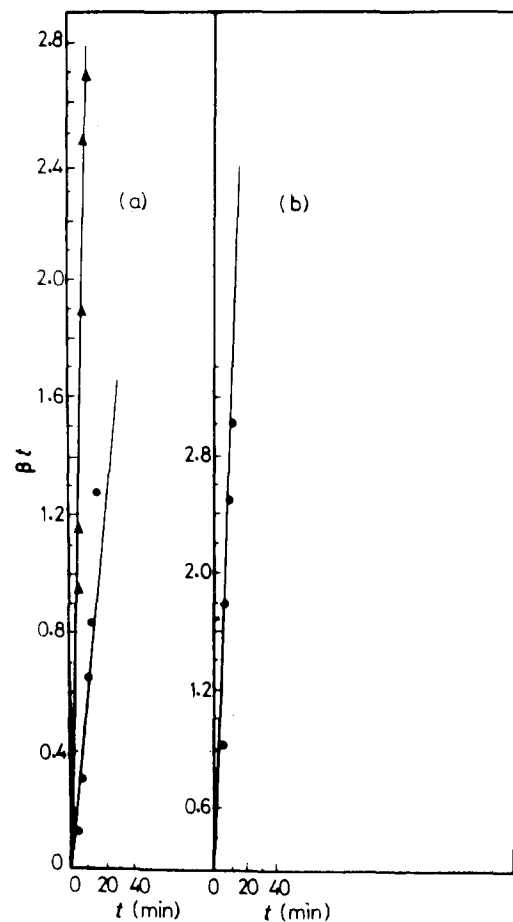


Figure 3  $Bt$  plotted against  $t$  plots (a) ▲  $T_{H5}$  (-100 + 200) with 0.3 M  $Ni(NO_3)_2$ , ●  $T_{H5}$  (-100 + 200) with 0.2 M  $Ni(NO_3)_2$ ; (b) ●  $T_{H5}$  (-60 + 100) with 0.2 M  $Ni(NO_3)_2$ .

calculated effective diffusion coefficient to remain unchanged in the case of both particle sizes.

The kinetics of exchange of the  $Ni^{2+}$  ions was investigated on both series of titania gels and the data obtained are given in Table III. Observation of these data indicates that varying the particle size has a tangible effect on the rate of exchange, in addition, a rate of exchange independent of concentration provides sufficient evidence that a particle diffusion mechanism is partly, or completely, responsible for the rate of exchange.

#### 4. General discussion

Titanium oxide exchangers prepared from salt solutions and a suitable base (as precipitating agent) were

shown to result in some cases in the formation of a macromolecular gel (the ion exchanger with two types of hydroxyl ions on the surface). One hydroxyl group is assumed to be bound to one  $Ti^{4+}$  site (terminal OH) and the other to two such sites (bridged OH). The doubly coordinated OH groups were shown to be strongly polarized by the cations, thus loosening the bond to hydrogen and resulting in acidic character, whereas the singly coordinated OH groups exhibited basic character with a tendency for dissociation as  $OH^-$  ions (therefore, exchangeable for other anions) or to which a cation can be adsorbed by strong electrostatic attraction. Also in these exchangers a high pH of preparation was shown to lead to gels with high exchange capacities and also to a large number of exchangeable OH groups, whereas low pH of preparation was shown to lead to the formation of gels

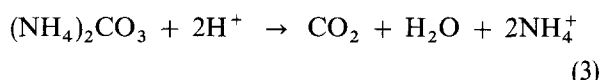
TABLE III Kinetics of exchange of the  $Ni^{2+}$  Ions on titania gels belonging to the  $T_C$  and  $T_H$  series

Sample	pH of preparation	Mesh size	Rate constant $B \times 10^3$ ( $s^{-1}$ )	Concentrations of $Ni^{2+}$ solution (M)
$T_{C8}$	8.0	-60 + 100	0.62	0.2
$T_{C8}$	8.0	-60 + 100	0.64	0.3
$T_{C8}$	8.0	-100 + 200	0.47	0.2
$T_{C5}$	4.7	-60 + 100	0.69	0.2
$T_{C5}$	4.7	-100 + 200	0.33	0.2
$T_{H5}$	5.0	-100 + 200	3.89	0.2
$T_{H5}$	5.0	-100 + 200	3.40	0.3
$T_{H5}$	5.0	-60 + 100	1.00	0.2

with low exchange capacities because of minimal exchangeable sites [8].

The results obtained in the present investigation with the  $T_H$  series of gels (oxidized by  $H_2O_2$ ) are in keeping with the above considerations. Moreover, in alkali precipitated gels, increase of pH usually produces a wider pore system, which we believe, should facilitate the exchange process within the pores. This is evinced by the steady increase in exchange capacities with increasing pH of precipitation reported in Table I.

In the case of the  $T_C$  series of gels, the unusual lack of variation of the exchange capacities with increasing pH of preparation could possibly be accounted [13] for by considering the following reaction involved in the preparation



In such a mode of gelation the hydrous titanium oxide is generated in a medium, which, from the onset, is very rich in  $NH_4^+$  ions.

It might, therefore, be expected that, by virtue of such a high concentration of  $NH_4^+$  ions in the precipitating medium, as in gels  $T_{C8}$  and  $T_{C5}$ , these would become entrapped within the three-dimensional network of the precipitated gel and may even lead to a gel that is predominantly in the ammonium form as opposed to the hydrogen form.

Indeed, in spite of the severe washing conditions of these gels (Section 2) infrared spectra clearly indicated that large quantities of  $NH_4^+$  ions are still entrapped. This is in accord with the fact that increasing the pH of precipitation did not result in an obvious increase in exchange capacities (Table I). Moreover, the microporosity does not seem to be appreciably affected by pH of preparation and contrary to the mesoporous gels, narrower pores seem to be produced by increasing the pH of preparation. This abandons any enhancement in the exchange process that might appear as a result of pore widening similar to the case with  $T_H$  series. It is, therefore, assumed that in the case of the  $T_C$  series of gels, it is the bulk concentration of  $NH_4^+$  ions generated by the interaction of  $(NH_4)_2CO_3$  with the acidic titanous chloride that is a basic contributing parameter in terms of exchange capacities. Meanwhile the microporous texture of this series of gels also appears to have a significant role in the exchange capacity data due to molecular sieve effects. It is also noticed that the presence of  $Cr^{3+}$  in the hydroxo complex form seems to inhibit its exchange with the appropriate surface species.

The drastic decrease in these gels of the 1400 and 1440  $cm^{-1}$  infrared bands (attributable to  $NH_4^+$  ions in different sites) upon immersion in the  $Ni(NO_3)_2$  solution with the intensity of the hydroxo band remaining virtually unchanged, corroborates such an interpretation. The same effect was observed with the  $Cr(NO_3)_3$  solution but accompanied by a decrease in the 1110  $cm^{-1}$  band characteristic for basic terminal OH groups. This, together with the observation of the existence of  $Cr^{3+}$  in the hydroxo form, shows that the

process of exchange or uptake in this case is more complicated and other factors seem to interfere.

The striking similarity between the infrared spectra of the ammonia immersed  $T'_{C8}$  gel and that of gels  $T_{C8}$  and  $T_{C5}$  is also in accord with the above interpretation. Here the total conversion to the ammonium form has been brought about in the case of gel  $T'_{C8}$  through immersion in  $NH_4OH$ , whereas in the case of gels  $T_{C8}$  and  $T_{C5}$  conversion to the  $NH_4^+$  form has resulted from a bulk generation of ammonium ions during the initial stages of the gel preparation.

The presence of  $NH_4^+$  ions in the present titania gel exchangers also seems to provide additional clues in the understanding of the kinetics of exchange bearing in mind that in these systems particle diffusion was probably the rate determining step as was shown earlier.

The much higher rates of exchange observed in the case of the  $T_H$  series of gels as compared to the  $T_C$  series may, however, arise from two possible effects. In a way, it may indicate that in the latter case (if the suggestion that the exchangers are in the  $NH_4^+$  form is correct), a slower rate of exchange would possibly result from steric effects due to the presence of the  $NH_4^+$  ions. Exchange with the  $H^+$  ions in the case of the  $T_H$  series of gels would be expected to take place much more readily. On the other hand, the texture of the gels seems to have a role in determining these rates. In the case of particle diffusion kinetic studies the surface texture is thus an undenied contributing parameter to the exchange rates. Since series  $T_H$  is known to be mesoporous whereas series  $T_C$  is microporous then the increased potential fields of force [28] within the micropores retards the movement of the cations to be exchanged with the pore surface species and thus a lower rate is observed.

Table III also indicates that for the  $T_H$  series of gels, increasing the particle size causes, as expected in conventional ion exchange reactions, a decrease in the rate of exchange.

In the case of the  $T_C$  series of gels, increasing the particle size leads to an increase in the rate of exchange which is in accordance with our belief in the retarding effect occurring in the micropores. Nancallas and Patterson [29] have observed a somewhat similar state of affairs on studying the kinetics of  $Na^+ - H^+$  exchange on zirconium phosphate.

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*Received 5 June 1990  
and accepted 31 January 1991*