Intercalations on α and gamma-Or-phosphate

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الخلاصة

:تفاعل فوسفات الزكونيوم ذات التركيب الكيمياوي على شكل طبقات مع مكبات مثل الكحولات والامينات,تمت متابعة التفاعل بواسطة تقنية طيف الاشعة السينية وظهر ان المسافة العمودية بين الطبقات يمكن زيادتها حتى تصل الى حدود 40انكلستروم وحسب عدد ذرات الكاربون في تركيب الامين او الكحول

مما يؤيد استخدام هذه المركبات الفوسفاتية في الامتزاز الكيمياوي حيث يمكن ازالة اثار الامتزاز بالغسل بالماء المقطر تمتاز المركباتنم نوع الكيل الامين بانها اكثر ثباتا من الكحولات الممتزة بين طبقات الفوسفاتولا تزال الا بعد تسخينهابين 200-300 م ,هذا النوع من الامتزاز يمكن ان يعطينا معلومات حول استخدام هذه المركبات بالاغشية الرقيقة .

Introduction:

The intercalation of layered crystalline structures of some thoroughly investigated synthetic inorganic ion exchangers of some insoluble acid salts of tetravalent metals of general formula $M(IV)(HXO_4).nH_2O$ where(M(IV)=Ti,Zr,Ce,Sn and X=P,As) have a layered structure, such layer consisting of a plane of tetravalent atoms sandwiched between tetrahedral phosphate or arsenate groups.

The bonds within the layers are strong and primarily covalent those between adjacent layers are week, essentially Vander Walls Fig(1),consequently, the layers can move in relationship to each other when protons are replaced by other cations or when the number of water molecules changes due to this ability, layered acid salts of tetravalent metals posses the typical characteristic of an intercalating agent.[1,2] written on Zirconium phosphate that has a number of superior properties compared with other intercalating compounds ".Layered insoluble acid salts generally have a higher thermal stability.[3,4]

Furthermore, the presence of acid groups between the layers make these exchange very suitable intercalating agents of polar molecules that are Bronsted bases[3], Layered phosphates and arsenate of tetravalent metals resemble natural clays.

The intercalations of guest molecules with the host matrix must be stronger than the mutual intercalation of the molecules with themselves or with the solvent molecules when they are dissolved. Thus, the surface of the layers of the intercalating agent should posses active sites or groups that can act as Bronsted acid,Lewis acid,[5,6] etc, or that, generally, have a polar character., with which the quest molecules can interact.

The layers must separated apart to accommodate the quest molecules. thus the interlayer bonding must be weak and the stacking of the layers should be such as to not create steric hindrance to the free diffusion of the molecule. Owing to the steric hindrance the intercalation process requires an activation energy.[7]

When the number of the molecules taken up per formula of intercalating agent is equivalent to the number of the active site present, intercalation compound with tachometric composition are obtained, this compound are not formed if the cross diameter of the guest molecule exceed the free area around the active site;" covering effect" of adjacent sites by the guest molecules may in fact take place and sites, partially or completely covered ,are unavailable to other molecules[8].

X-RD ,examination of α-type structure give table (1).Formula, Interlayer Distance and Calculated Surface area, associated with the active sites of α and gamma-Zr-phosphate structure.

Compound	Interlayer distanced,(A^0)	Free area around the active site(A^2)
alpha-$Zr(HPO_4)_2.H_2O$	7.55	24
Gamma-$Zr(HPO_4)_2.H_2O$	11.6	16.7

The action density between the sheets is very high,(2 eq.per formula unit) ,strong Columbic force holds the layer together; intercalation should occur with great difficulty and ,for the α- type the action density is equal to 1 esq. per formula as if one-OH out of two dissociated.
However, more both the protons are covalently bonded to the Oxygen atoms. Thus a much smaller action density is to be expected and this was born out by measurements of specific conductance of the crystals, hydrogen forms of layered acid salts are indeed able to intercalate polar molecules.[9]
The active sites are P-O-H groups which are Bronsted acids.
These are regularly arranged in hexagonal arrays at 5.3A away from each other in alpha-Or-phosphate it is similar to create Zeolitic cavities that interconnected by narrow openings. The diameter is 2.61A,that the satiric hindrance and hence an activation energy for the process must be overcome. These molecules having across section higher than this value will give way to the "covering effect".[10]

Gamma-type ($12.3\,\overset{o}{A}$) much higher than that of α –type($11.7A^0$),then intercalation occur more easily.
Gamma-type is more dense structure than α –one, this produce an area of the exchange sites is smaller than α-compounds and covering effects may also take place with the intercalation of n-alkyl amines.
The intercalation process in layered phosphates occur discontinuous usually with phase transitions almost exactly as described for the ion exchange processes.
XRD-analysis give rise of the d_{100}reflections this relative to the basal spacing of the host matrix, is shifted to higher value and harmonics up to high order may be detected .Fig.(2),the observations on the spectrum sample ,the presence of two diffraction peak corresponding to the interlayer distances of the original and the new phase transition in the intercalation process of polar molecules within the layers of insoluble acid salts very likely proceeds from the external parts of the crystal towards the center with advancing phase boundary, until the fully intercalated compound is completely obtained, during the intercalation, the intensity of former XRD,reflection decreases and that of later increases ,as if two phases, the one transforming into the other, were coexisting.[11] This above mentioned observations, let us now examine some data on the intercalation behavior of layered phosphates
Procedure. $\alpha - Zr - phosphate$ like $ZrHNa(PO_4)_2.5H_2O$ prepared as mentioned in the reference[1,16] is putting at room temperature for 24h. with contact with 0.1M of protenated alkanols solutions, which act as Bronsted acids.
The reaction between the mono Sodium form and alkanols protenated with HCLO,viz:
$ZrHNa(PO_4)_2.5H_2O+R\text{-}O^+H_2+XR\text{-}ZHr(HPO_4)_2.(1+X)ROH+Na+5H_2O$
Where R=n-alkylchain,leads to intercalation compound of α-Zirconium phosphate.,[4] the reaction above fails when R is long or branched alkyl-chain or contain the benzene ring,e.g, C_8H_{17}, $CH_3)CHCH_2CH_2$-,C_6H_5-CH_2—but once one alkanol- interacted compound has been obtained by the reaction above, it is easy to replace the intercalated molecule e,g,C_2H_5OH with other alkanopls by simply contacting the Zr-phosphate-ethanol complex with the pure liquid to intercalated. we are obtain a number of Zr-phosphate-alkanol intercalation compound with these two methods they are listed in table(2).

Intercalated molecule	Method of preparation	Inter layer distance,d,A^o	Increment, Δ ,A^o	
Methanol	1	9.3	d-6.3	d-9.1
Ethanol	1	14.2	7.9	5.1
1-Prpanol		16.6	10.3	7.5
1-Butanol		18.7	12.4	9.6
1-Pentanol		21.3	15.0	12.2
1-Octanol		26.7	20.4	17.6

(Method:1=equilibration of $ZrNa(PO_4)_2$ with protenated alkanol or glycol

2=equilibration of Zr-phosphate- ethanol complex with the alkanol or glycol).

The complex of n-alkanol-Zr-phosphate contain 2 moles of intercalated molecule per mole of exchanger. In the case of isoalkanols or branched alkanols,the "covering effect" should prevent the obtaining of stoichiometric compounds ,this preparations having different degrees of crystallinity or different size could lead to different kinetic effect and, in this case ,to obtain more easily an intercalation compound. The stability of glycol-Zr-phosphate compounds are higher than that of alkanol ones.

Zr-phosphate-alkanol compounds may be considered as very good starting materials for the intercalation of other polar molecules.[12]

In fact, the interlayer distances of these compounds are very large, and no steric hindrance obstructs the diffusion of polar molecules within the layer of the exchanger, further more, alkanols are held with weak forces to the layers and can easily be replaced by other polar molecules. such as acetonitrile,acetylacetone,dimethyle acetone,etce, have been easily intercalated in α-Zr-phosphate simply by contacting the methanol or ethanol intercalated compound with the corresponding pure liquids to be intercalated., dispersion in water give rise to the poly hydrated hydrogen phase with an inter layer spacing of $10.4A^0$,and the ethanol-Zr-phosphate is more effective complex for obtaining inter calation compounds than the methanol one accuse to its inter layer distance $14.2A^0$,[2]were able to obtain similar intercalation compound by contacting α-Zr-phosphate with a concentrated aqueous solution in the case of solid guest molecule. The increase in the basal spacing ,(d) ,is equal to the diameter of the intercalated molecules ,water molecule diameter is $2.8A^0$,that leads to conclusion that these molecules replace the water molecules in the cavities of exchanger.[13]

Owing to the tetrahedral –POH groups within it s layers, Zr-phosphate shows a high preference for strong bronsted bases such as ammonia and amines, which are easily intercalated from diluted solutions and, in some cases also from vapor phase. Zr-phosphate –methanol complex, dispersed in water or in methanol containing the amines to be intercalated, has been used successfully, this is regarded as the protenation of amines with – POH groups of exchanger. has been demonstrated that the conversion of α-Zr-phosphate into diammonium form results from the diffusion of free NH_3 between layers and it is promenaded, according to the reaction,

$Zr(HPO_4)_2.H_2O+2NH_3 \rightarrow \quad Zr(NH_4PO_4)_2.H_2O.$

Table(4)shows the interlayer distance and ratio of intercalation compounds of α-Zr-phosphate with several amines. It has already been pointed out that the intercalation of amines may be performed by titrating the exchanger suspended in water , with dilute solution of free amines,ethylinediamine and pyridine, Fig(3)resemble the titration curves obtained shows different steps at various PH values, in each step of the titration curves two intercalates are generally coexisted, one transforming in to the other as the intercalation process proceeds,[14] while in the sloping region of the curves only ones present. thus ,the intercalation process occurs discontinuously, with phase transition, it is not easy to see the number of steps in which the process occurs since it seems to depend on the basicity of the molecule, the length of the alkyl chain, the possible configuration of the guest molecules within the layers, the water content of the intercalated and so on..

Titration curves of α-Zr-phosphate with pyridine and butylamine have been reported, In the case of pyridine, the curve showed only one end point and the phase $Zr(C_5H_5NHPO_4)_{0.45}(HPO_{41.55}.H_2O$(inter layer distance $10.9A^0$)was identified.

Only 25%of active sites of exchanger are saturated by pyridine,[15] and this fact has been explained by considering the weak basic character of the molecule and assuming that α_-$Zr(HPO4_{)2}.H_2O$ has different kinds of acidic sites under suitable experimental conditions higher uptakes of pyridine are however expected, .The potentiometric titration curve with n-Butylamine shows two plateaus, the first ranging from 0 to 5 m.mol of n-Butylamine added Fig(3), the second from 5 to 7.

The phases $Zr(C_4H_9NH_3PO_4)_{1.34}(HPO_4)_{o.66}.0.95H_2O(d=18.2A^0)$ and $Zr(C_4H_9NH_3PO_4)_2.H_2O$,in addition, it was found that at an amine uptake of about 1.0m.mol/g the original α-$Zr(HPO_4).H_2O$

was converted in a mixture of two phases, whose inter layer spacing were $10.5A^0$ and $18.2A^0$.The phase $10.5A^0$was found to disappear at slightly higher loading and up to the amine content of 4.0m.mole/g, the $7.6A^0$α-$Zr(HPO_4)_2.H_2O$) and $18.2A^0$ phase were found.

$Zr(HPO_4)_{2)}(\text{Butyl amine})_{1.33} \xrightarrow{0.67 Butyla\min e} (Zr(HPO_4)_{2)(\text{Butyl amine})}2$, $d=18.8A^0$

The titration curve obtained for the intercalation of propyl amine, was found to be much more complicated .the phase with interlayer spacing of $10.5A^0$ is formed at uptake lower than 0.5m/mol/g.

The relative percentage of this phase increased as amine was further intercalated,Recrystallization occurred at about 4.5 m.mol/g to yield three intercalated phases with inter layer spacing of $14/6A^0$,16.4,and$17.3A^{0.}$

$Zr(HPO4)_2 \xrightarrow{propyla\min e} (Zr(HPO_4)(\text{propyl amine}) \xrightarrow{propyla\min e} (Zr(HPO_4{}^)2^{)(\text{propyl amine})}$

$7.6A^0$ $10.5A^0$ $17.8A^0$

The fully intercalated phase having the composition's$(C_3H_7NH_2)_2(HPO_4)_2.H_2O$ with interlayer distance=$17.8A^{0.}$

An interesting series of phase transitions was found in the intercalation process. the titration curves of methylamine, ethylamine, propylamine,and butylamine are shows in fig (3). the alkyl chai may incline to the layers at an angle of less than 60^0.thus in the

first stage of the intercalation process, the alkyl chain may lie parallel to the layers, and the phases with interlayer distance $10.5A^0$have been attributed to the presence of that arrangement as the intercalation increases the amine chain are forced in to amore upright position and "kind" and "gauch"arrangement of the alkyl chain may take place before the final orientation in the fully intercalated compounds is reached.

INTERCALATION BEHAVIOR OF GAMMA-Zr- PHOSPHATE:

The gamma-Zr-phosphate and gamma-Ti-phosphate have been identified to have gamma-structure ,the higher value of the interlayer distance, suggests that gamma-phase are better able to intercalate polar molecules than α-one. table(3)are listed the interlayer distances of some compound this must be noted that intercalation of alkanols and molecules with weak basic character occurs by simply contacting the exchanger with the pure liquid to be intercalated, the interlayer spacing increase almost linearly with the increasing number of carbon atoms in the alkyl chain, and it may be supposed that diamines form a unimolecular film while alkanols or alkylamines give rise to bimolecular film asin α-phase.Table(3)Interlayer distance d,of intercalation compounds of gamma-Zr-phosphate and with various kinds of polar organic molecules.

Intercalated molecules	Gamma-Zr-$(HPO_4)_2.2H_2O$ (interlayer distance ,d A^0		
Methanol	12.7	butylamine	15.9
Ethanol	16.6	decylamine	21.5
Hexanol	24.9	propanol	33.4
2-propanol	19.4	butanol	33.4
Ethyleneglycol	13.4	octanol	20.0
Dimethylsulfoxide	16.2	ethylamine	21.5
Acetone	14.4	heptylamine	30.
N,N-dimethylformamide	16.5	ethylenediamine	18
N-methylformmidee	15.9 12.5 18.0	heptmethylenediamine	25
Urea	13.6	decamethylenediamine	20.5

This table shows that the increase in basal spacing is about equal to the diameter of guest molecules minus 2.(diameter of water).and alkylamines,whose cross-sectional diameter is evaluated as $4.4A^0$,present "uncovering effect", the gamma-Zr-phosphates have amore open interlayer space than

α-ones and hence present lower satiric hindrance to the diffusion of the alkanols within the layers, the thickness of the gamma-type ia 9.5$A^0$and for α- type is 9.2A^0,when we plot the number of carbone atoms present in the alkyl-chain (n)against the d in A^0we get linear relationship between the two coordinate fig(5),d ,distance increase from 3to 3.6A^0/carbon atom and the change in $\frac{\Delta d}{\Delta C}$ gradient may be attributed to changes in the composition of the film or to the change in the orientation of the intercalated molecules with the increase of the alkyl chain length. The increase in the basal spacing, when the alkyl chain length ranges from C_4 to $C_8$is consistent with the presence of double layer of alkanols,incined with respect to the sheets of angles lower than 55^0,this may be attributed to different orientation of $–CH_2OH$ terminal groups of the alkanols in the faces of the layers of exchanger.

The above observation lead to the conclusion that alkanols intercalated in gamma-Zr-phosphate result in arrangement less organized than that found for α-one, and the gamma-Zr-phosphate may be achieved by titration of these molecules with the exchanger with dilute solutions of amines to be intercalated. Fig(4),illustrates the potentiometric titration curve obtained by titrating 0.5g of gamma-Zr-phosphate dispersed in 50ml of water, with 9.1m propylamine solution .the titration curves yield a good information about the capacity of exchange and the mechanism of intercalation process, Table (4) shows the interlayer distance of some intercalated gamma-Zr-phosphate with n-alkylamines and diamines with respect to the composition of the intercalated compound.

Amines And diamines	Gamma-Zr-phosphate	
	D(A^0)	Composition
Ethylamine	15.3	1.05
Propylamine	17.6	0.95
Butylamine	19.2	1.00
Decylamine	33.4	1.05
Dodecylamine	37.4	1.42
Tetradecylamine	40.5	1.33
Hexadecylamine	44.0	1.33
Octadecylamine	47.7	1.33
Ethylinediamine	12.4	0.53
Tetramethylidiamine	14.7	0.51
Tetraethylinediamine	22.0	0.48

Table(5) shows the d,in$A^0$with the composition of intercalated compound of Zr-phosphate with n-alkylamines

Zr-phosphate	$C_nH_{2n+1}NH_2$	mH_2O	$D_{001}(A^0)$
n	x	m	
3	0.55	1.4	21.31
4	0.58	1.5	22.50
5	0.60	1.6	24.02
8	0.61	1.2	29.47
10	0.60	1.1	31.70
12	0.61	1.1	34.96

It is expected that the bilayers formed in gamma-Zr-phosphate compounds, and the conformational changes in the alkyl chains and hence the phase transitions in the structures of the

bilayers,thus may be considered a good models for studding of the formation and the properties of the bilayers as well as the phase transitions induced
thermally or by the variation of the electrolyte concentration.

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