Uptake of Some Divalent Metal Ions on Layered α-VOPO4.2.5H2O and Its 1,10-Phenanthroline, 2,2′-Bipyridyl and 4,4′-Bipyridyl Intercalated Products

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Abstract

The crystalline layered α-vanadyl phosphate, α-$VOPO_4.2.5H_2O$, was prepared and characterized. Its intercalated products $VOPO_4(1,10\text{-phen})_{0.33}.0.6H_2O$, $VOPO_4(2,2^{'}\text{-bipy})_{0.36}.0.25H_2O$ and $VOPO_4(4,4^{'}\text{-bipy})_{0.4}$, were prepared by direct contact of α-$VOPO_4.2.5H_2O$ with 0.1M organic ligand in ethanol with stirring for 7 days at room temperature. The resulting products were characterized by chemical and thermal analysis. The distribution coefficients (Kd values) for a mixture of 0.05M nitric acid solution of the divalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} were determined simultaneously by (ICP) technique after equilibration with $VOPO_4.2.5H_2O$ and its intercalated products at pH 2 and 4. The (Kd values) for Pb^{2+} ions were higher than those for other metal ions, especially at pH4. Possible selective separation of Pb^{2+} is quite evident. The selectivity order was found to be dependent on the pH and on the nature of the intercalated ligand. Partial ligand release of intercalated products at pH 2 observed.

Introduction

Oxovanadium (V) phosphate can be considered as a chemical precursor for other oxovanadium (IV) or (V) compounds[1,2]. The latter compounds are found to be good catalysts for the oxidation of hydrocarbons and for selective oxidation of n-butane to maleic anhydride[3].

The abundance and low cost of light alkanes have generated in recent years considerable interest in their oxidative catalytic conversion to olefins, and nitriles in petroleum and petrochemical industries[3-6].

One of the most fascinating and unique catalytic processes is the 14- electrons[7] selective oxidation of n-butane to maleic anhydride (2,5-furandione) by vanadyl phosphates. It is the only industrial process of selective vapor- phase oxidation of an alkane that uses the dioxygen [7].Since 1974 n-butane has been increasingly used instead of benzene as the raw material for maleic anhydride production [8]. At present

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more than seventy percent of maleic anhydride is produced from n-butane[9]. Many studies on n-butane oxidation by vanadyl phosphate catalysts indicate that crystalline vanadyl(IV) pyrophosphates are present[10-13] in the most selective oxidation of n-butane to maleic anhydride.

α-Vanadyl phosphate, α-$VOPO_4.2.5H_2O$, is a well characterized compound that crystallizes in tetragonal system and it intercalates organic and inorganic cations by means of electron transfer system host lattice and a reducing agent[14,15].

Intercalation of heterocyclic organonitrogen compounds with layered structure has received considerable attention [16,17].

Novel pillared M (IV) phosphates derived from reactions of layered M (IV) phosphates with complex compounds attract attention recently for their possible applications as new ion-exchangers, catalysts and in photochemistry [18-20]. However the composition of the intercalate compound does not correspond to a complete solid host stoichiometric addition or neutralization since the product composition arises from "covering effect" of the guest molecule[21].

It was found that bulky amines such as 1,10-phenanthroline and 2,2′bipyridyl tend to intercalate with the metastable alcohol form of α-Zirconium phosphate, $Zr(HPO_4)_2.2C_2H_5OH$, to give α-$Zr(HPO_4)_2(Phen)_{0.5}.2H_2O$ and α-$Zr(HPO_4)_2(2,2′-bipy)_{0.25}.1.5H_2O$.[22] Recently it was shown that gamma zirconium phosphate, γ-$Zr.PO_4.H_2PO_4.2H_2O$, can intercalate with alcohol solution of 1,10-phenanthroline and 2,2′-bipyridiyl to give γ-$Zr.PO_4.H_2PO_4(Phen)_{0.5}.3H_2O$ and γ-$Zr.PO_4.H_2PO_4(2,2′-bipy)_{0.48}.0.3H_2O$, respectively.[23] Generally the intercalation mechanism of layered zirconium phosphates with amines is of acid-base type in which phosphate sites, the P-OH groups, act as acid[22-24.]

Recently, crystal structure of $[VO(HPO_4)(1,10.phen]_n$ has been reported. The structure consists of bis (vanadyl hydrogen phosphate) skeleton that assumes linear ribbon conformation. The nitrogen heterocyclic that chelate to the V(IV) atoms are connected to the hides of the feat-Ribbon[25].

This paper reports the preparation and characterization of α-vanadyl phosphate, $VOPO_4.2.5H_2O$, (α-VP), and its intercalated 1,10-phenanthroline, 2,2′- and 4,4⁻- bipyridyl products, and their uptake of some divalent metal ions on α-VP and its intercalated products at pH 2 and pH 4. This study lead to products which can be utilize as new inorganic ion-exchangers and as catalysts.

Experimental

Chemicals

The chemicals used were V_2O_5, H_3PO_4(85%), 1,10-phenanthroline, 2,2′-bipyridiyl and 4,4′−bipyridyl(products of BDH). Other chemicals used were of analytical grade

Preparation of $VOPO_4.2.5H_2O$

The layered α-vanadyl phosphate, α-VOPO$_4$.2.5H$_2$O was prepared by refluxing 10 grams of V$_2$O$_5$ in 37ml H$_3$PO$_4$ (85%) and 240ml of distilled H$_2$O with stirring for 24hrs[14]. The resulting precipitate was filtered, washed with cold ethanol (10°C) and air drying. The product was characterized by x-ray and thermal analysis and designated as compound (I).

Intercalation Procedure

1,10-phenanthroline, 2,2$'$-bipyridyl and 4,4$'$-bipyridyl intercalated products, VOPO$_4$(Phen)$_{0.33}$.0.6H$_2$O, VOPO$_4$(2,2$'$-bipy)$_{0.36}$.0.25H$_2$O and VOPO$_4$(4,4$'$-bipy)$_{0.40}$ respectively, were prepared from direct contact of 2 grams of VOPO$_4$.2.5H$_2$O with 130 ml of 0.1M of the organic ligand in ethanol at room temperature and with stirring for 7 days followed by filtration, washing with ethanol and air drying. The resulting intercalated products were characterized by chemical and thermal analysis and designated as compound (II,III and IV). The filtrate of compounds (II) and (III) were kept for the estimation of unreacted 1,10-phenanthroline and 2,2$'$-bipyridyl.

Estimation of the unreacted 1,10-phenanthroline and 2,2$'$-bipyridyl was carried out by addition of each filtrate to 12ml 0.05M (NH$_4$)$_2$Fe(SO$_4$)$_2$- .6H$_2$O in aqueous solution, followed by estimation of the absorption of the resulting Fe(phen)$_3^{2+}$and Fe(bipy)$_3^{2+}$ complexes using spectrophotometer at λ=508 nm. The concentration of the ligand were obtained from standard curves of the Fe^{2+} complexes.

It is known that mixing stoichiometric of Fe^{2+} with three molecules of 1,10-phenanthroline and 2,2$'$-bipyridyl in aqueous solution the reaction goes to 100% products of (phen)$_3^{2+}$and Fe(bipy)$_3^{2+}$ complexes. On that bases standard solution of (phen)$_3^{2+}$and Fe(bipy)$_3^{2+}$ were accurately prepared by mixing 0.1 M of the organic ligands (L) solutions with 0.05M (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O in the ratio of Fe: L (1:3) from that the standard curves were prepared using spectrophotometer at λ=508 nm.

The Equilibration Experiments

The aliquot were prepared by the addition of 30ml of the mixture of 0.05M nitric acid solution of divalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}, of pH 2 and 4 at each time, (5ml of each metal ion solution) to 0.1g of α-VOPO$_4$.2.5H$_2$O, (α-VP), and similarly were carried out with 0.1g of the intercalated products that were equilibrated for 48hrs. at room temperature under shaking.

The Kd values of equilibrated divalent metal ions were determined simultaneously using (ICP) technique (Spectroflame Modula, industrial research center, Tripoli).

X-ray diffractogram were recorded on Siemens D500 Diffractometer using Ni-filter CuK$_\alpha$-radiation (λ=1.54056 Å). Thermal analysis were carried out with Thermogram MOM-C Budapest for VOPO$_4$.2.5H$_2$O and by Seiko thermal analyzer, (industrial research center, Tripoli) for the intercalated products. Ligand estimation was carried out with UV Spectrophotometer spectronic21D.

Results and Discussion

Crystalline layered α-VOPO$_4$.2.5H$_2$O was prepared and characterized by x-ray and thermal analysis. Its x-ray powder diffractogram is shown in (figure 1) from that its interlayer distance was found to be equal to 7.22 Å.
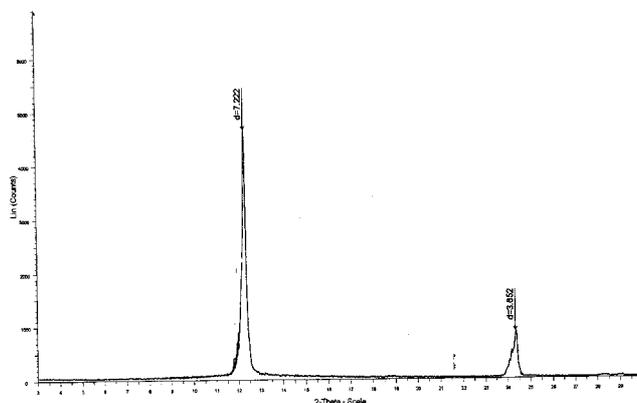

Figure 1. X-ray diffractogram of α-VOPO$_4$.2.5H$_2$O

(Figure 2) represents the thermogram of VOPO$_4$.2.5H$_2$O. Thermal analysis was carried out at the range of~35- 900°C. The loss of water of hydration occurs in two steps with two endothermic peaks at 125°C and 175°C. Endothermic peak at 740°C accompanied by weight loss equal to 3.12%. The total weight loss found to be equal to 24.85% which is almost equal to the calculated value 25.1%, accordingly it was formulated. The final product found to be (VO)$_2$P$_2$O$_7$.
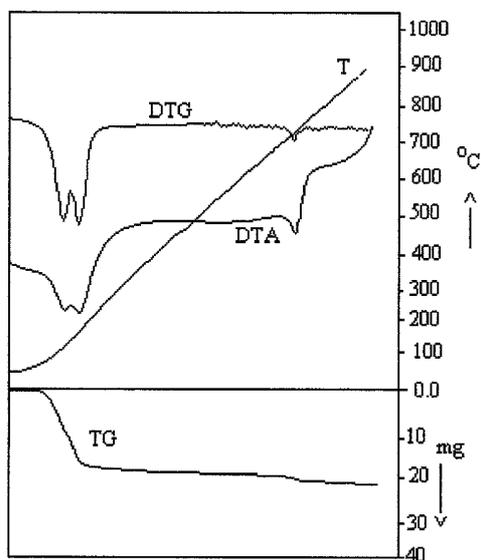

Figure 2. TG/DTA of α-VOPO$_4$.2.5H$_2$O

From reaction of α-VOPO$_4$.2.5H$_2$O with 0.1M 1,10-phenanthroline 2,2$^{'}$-bipyridyl and 4,4$^{'}$-bipyrydyl in ethanol at room temperature. The intercalated products VOPO$_4$(1,10-phen)$_{0.33}$.0.6H$_2$O, VOPO$_4$(2,2$^{'}$-bipy)$_{0.36}$.0.25H$_2$O and VOPO$_4$(4,4$^{'}$-bipy)$_{0.4}$

were obtained respectively, and were designated as compounds II,III and IV respectively. The intercalated products were characterized by chemical and thermal analysis. Figures 3-5 show the thermograms of 1,10-phenanthroline, 2,2′-bipyridyl and 4,4′-bipyridyl intercalated products.Their thermal analysis were carried out at the range ~28-845°C The weight losses (TG) curves as a function of temperature and (DTA) curves show the endothermic process, from that the resulted intercalated products were formulated. In all cases the final product is $(VO)_2P_2O_7$.

Although there are few reports about thermal analysis of α and γ M(IV) phosphates and their amine intercalated products[26-27]. To date there are no reports about thermal analysis of organonitrogen intercalated products of vanadyl phosphates.

Thermal analysis is a promising field for characterization of M(IV) and their intercalated products[26-28]. correlation between thermal analysis and chemical analysis data that obtain for M(IV)phosphates and their intercalated products show to support the idea that thermal analysis is a good tool for formulation of such type of products.

(Figure 3) shows the thermogram of compound (II), 1,10-phenanthroline intercalated product. Its thermal decomposition found to occur in three stages. The dehydration stage occurs at temperature range ~80 -160°C followed by deintercalation and decomposition of the organic ligand. The final product was $(VO)_2P_2O_7$, the decomposition of the organic ligand found to superimpose to that due to formation of vanadyl pyrophosphate. The total % weight loss found to be equal to 34% and the calculated value is 33.69%.
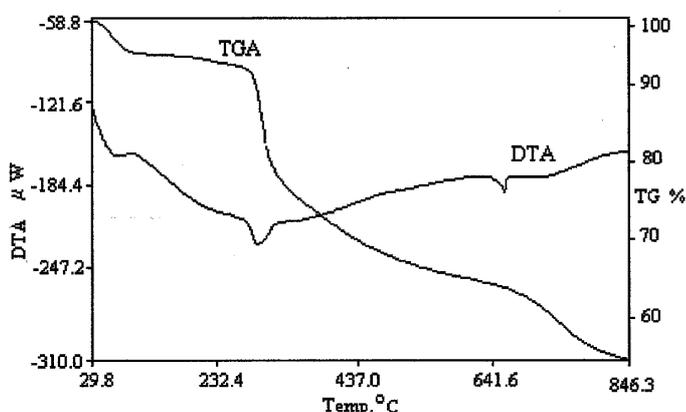

Figure 3. TG/DTA of α-VOPO$_4$ (1,10-phen)$_{0.33}$.0.6H$_2$O

Thermal decomposition of of 2,2′-bipyridyl intercalated product, compound (III),found to occur in four stages as shown in (figure 4). The dehydration stage occurs at temperature range ~100 –150 $^{\circ}$C, followed by deintercalation and decomposition of the organic ligand, the final product was $(VO)_2P_2O_7$.The decomposition of the organic ligand found to superimpose to that due to formation of vanadyl pyrophosphate, The total % weight loss found to be 31.1% and the calculated value is 30.89%.
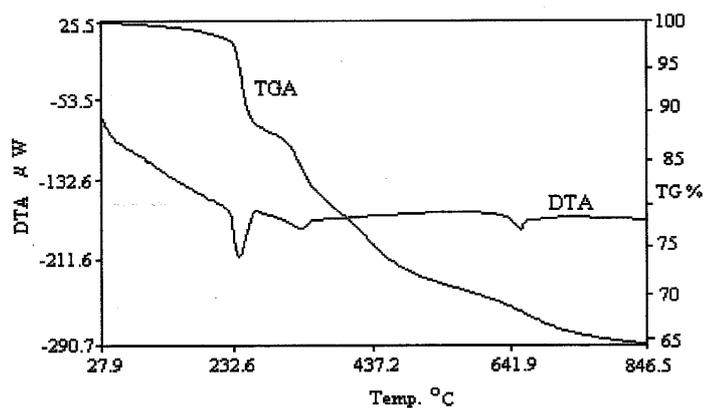
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Figure 4. TG/ DTA of α-VOPO$_4$(2,2′-bipy)$_{0.36}$.0.25H$_2$O

Thermal decomposition of of 4,4′-bipyridyl intercalated product, compound (IV),found to occur mainly in three stages as shown in (figure 5), started with deintercalation of the organic ligand at 180 $^{\circ}$C and followed by its decomposition stages. The final product was (VO)$_2$P$_2$O$_7$. the decomposition of organic ligand found to be superimpose to that due to formation of vanadyl pyrophosphate. The total % weight loss found to be equal to 31.29 % and the calculated value is equal to 31.38%.
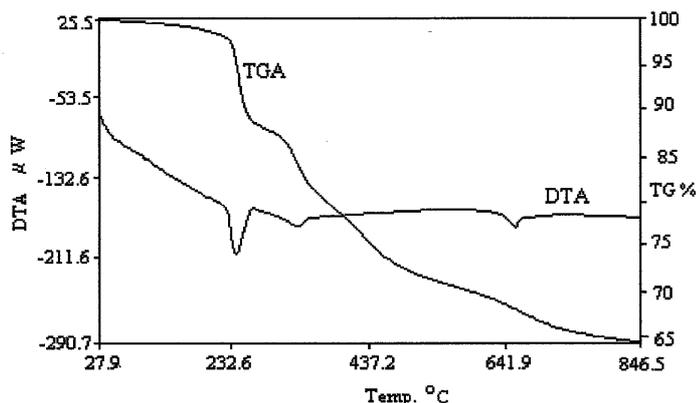

Figure 5. TG/DTA of α-VOPO$_4$(4,4′-bipy)$_{0.4}$

From thermal analysis total % weight loss and chemical analysis of the organic ligands loading the intercalated products were formulated.

Distribution coefficients (Kd values) that obtained from equilibration of the metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions with α-VOPO$_4$.2.5H$_2$O), and its intercalated products VOPO$_4$(1,10-phen)$_{0.33}$.0.6H$_2$O, VOPO$_4$(2,2′-bipy)$_{0.36}$.0.25H$_2$O and VOPO$_4$(4,4′-bipy)$_{0.4}$ at pH 2 and 4 of HNO$_3$ were determined simultaneously using ICP technique. The kd values are shown in (table 1, 2).

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Table 1. Selectivity (Kd-values) at pH2

α-VP	Pb(151.81)	Co(10.58)	Cd(10.25)	Zn(6.62)	Cu(6.07)	Ni(0.27)
VP(1,10-phen)	Pb(107.49)	Co(15.7)	Cu(11.81)	Zn(10.78)	Ni(9.26)	Cd(7.51)
VP(2,2′-bipy)	Pb(106.57)	Cu(39.84)	Cd(11.49)	Co(11.47)	Zn(10.04)	Ni(9.26)
VP(4,4′-bipy)	Pb(697.62)	Ni(30.0)	Cd(8.27)	Zn(5.90)	Co(5.34)	Cu(5.23)

Table 2. Selectivity (Kd-values) at pH 4

α-VP	Pb(343.91)	Cd(7.08)	Ni(3.52)	Co(0.55)	Cu(0.0)	Zn(0.0)
VP(1,10-phen)	Pb(366.45)	Ni(15.20)	Cd(14.34)	Cu(11.73)	Zn(10.89)	Co(10.18)
VP(2,2′-bipy)	Pb(382.51)	Cu(21.31)	Ni(12.85)	Cd(12.49)	Zn(6.97)	Co(6.71)
VP(4,4′-bipy)	Pb(2128.63)	Cu(14.0)	Ni(4.35)	Cd(4.0)	Zn(1.14)	Co(0.85)

From Kd values it can be seen that can see α-vanadyl phosphate, α-VOPO$_4$.2H$_2$O shows good selectivity for Pb^{2+} ions at pH2 and 4 equal to (151.81) and (343.91) respectively. The Kd values for the rest of the metal ions at pH2 and pH4 were quite low (<11).

For intercalated products, the Kd values for Pb^{2+} ions (107.49) and (106.67)at pH 2 (366.45) and (382.5) at pH4 were found for 1,10-phenanthroline and 2,2′-bipyridyl intercalated products respectively as shown in (tables 1, 2). However, the highest Kd values, for Pb^{2+} ions were found with 4,4′-bipyridyl intercalated product which were equal to (697.62) and (2128.63) at pH2 and pH4 respectively. For the rest of the metal ions the Kd values were low, as shown above.

In general we can say that the above materials can be utilize for selective separations of Pb^{2+} ions from the above mixture of metal ions. The selectivity order found to depend upon the pH, and on the nature of the organic ligand. However we can not rule out the possibility of some complex formation of the divalent transition metal ions, by the intercalated products by amine ligands. Partial ligand release at pH2 were observed, 14% for 2,2′-bipyridyl and 4% for 1,10-phenathroline and 4,4′-bipyridiyl intercalated products. In conclusion the resulted intercalated products can be utilize as new ion-exchangers and as new catalysts[29-31].

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