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A New Hybrid Material of Vanadoaluminophosphate templated by 1, 3-Diaminopropane

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Abstract

A vanadoaluminophosphate has been hydrothermally synthesized at 180°C, under autogenously pressure in the presence of fluoride anions and diaminopropane (D.A.P) as structuring agent. The VAPO-DAP material was characterized by: Powder X ray diffraction, FT-IR, S.E.M., Chemical and thermal analyses and NMR spectroscopy (^{27}Al, ^{31}P & ^{51}V). The following empirical formula agrees with the results of the characterization: VAPO-DAP = $[Al_5 P_5 V_{0.25} F_{1.4} O_{26}]^{2-}$ $[H_3N (CH_2)_3 NH_3]^{2+}$. The advantage of this method is that the pressure of the medium increases slightly under these conditions and this pressure can lead to crystallization phenomena at low temperatures for this type of material (<200 °C). It is also possibility of obtained metastable phases original inaccessible through “high temperature”, this is an interesting asset of this technique. This material has been tested by aerial oxidation of cyclohexane to cyclohexanol, in the growing field of solvent-free industrial reactions.

Keywords: Thermal analysis, Spectroscopy, aluminophosphates, vanadium, diaminopropane.

1. Introduction

Aluminophosphates synthesis was first initiated by Wilson and his coworkers in 1982 [**1**].
The success of their process has incited many scientists working in the same field to prepare substituted aluminophosphates using transition metals such as: V, Fe Mo, Ti, W, Ga, Zn, Co **[2-11].**

The incorporation of such metals gives rise to novel properties, potentially useful for various applications in catalysis, adsorption and ion exchange.

In this paper, we show the preparation of a new vanadoaluminophosphate by hydrothermal method.

2. Experimental

The title compound was synthesized by hydrothermal crystallisation of an gel obtained from aluminium, phosphorus, vanadium and fluoride sources, in the presence of water and an organic structure directing agent. The nucleation and crystallisation were carried out inside a hermetic 20 cm^3. Teflon lined stainless steel autoclave.

2.1 Starting Materials

The reagents used in this work were orthophosphoric acid (85 wt %) and hydrofluoric acid (40 wt%) were purchased from Fluka. Vanadium pentoxyde (99.9 wt%), 1,3- diaminopropane (D.A.P. 99.8 wt %) and Aluminium isopropoxide Al(Isopro)$_3$ (99 wt %), from Merck.

2.2 Synthesis procedure

The vanadoaluminophosphate was prepared in a Teflon lined stainless steel autoclave. The reactive precursor gel was prepared by adding, under stirring, the aluminium source to H_3PO_4 in water. After homogeneisation, the vanadium oxide was added and then, successively, HF and 1,3 diamino-propane were introduced. The initial molar composition of the gel was

1 H_3PO_4; 1 Al (Isopro)$_3$; 0.1 V_2O_5; 0.05 HF; 1.2 DAP; 100 H_2O.

The reaction mixture was stirred further until homogeneity was reached and then heated at 180°C under static conditions. After 48 hours of heating, the solid product was recovered by filtration, washed with distilled water until neutralization (pH = 6.5 - 7) and dried overnight at 60°C.

The pH in the reaction mixture is an important parameter for equilibrium and formation material. It determines their composition and is largely responsible for the type of the material **[12-17].** In general, crystallization passes through the liquid phase, so that the species present in the reaction medium are transformed to the state of oxo anions (aluminate, vanadate, ect.). These species in the solution favor the mechanism of crystallization. pH measurement is recommended before and after crystallization, $pH_{before} = 8.19$; $pH_{after}= 10.05$.

2.3. Instrumentation

The phase analysis of a powder sample was carried out in a Brucker D8 diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å), Laboratory of Materials Science-USTHB-Alger. The structural analysis was studied using a diffractometer KAPPA CCC, scan type: φ and ω scans, performed in the Crystallography Centre of Lyon 1-France. Solid-state ^{31}P NMR, ^{27}Al NMR & ^{51}V NMR spectra were recorded on a Bruker DSX 300 Ultrashield spectrometer. The 4 mm MAS probe used a rotation speed of 8 kHz. The field frequencies were 78.2 MHz for ^{27}Al and 121.5 MHz for ^{31}P. Aluminium spectrum was recorded with a pulse time of p/10 (0.5 μs) and a recycle time of 1s and Phosphorus spectrum with a pulse time of p/2 and a repetition time of 1s, Catalyse Centre of Lyon -France. Thermogravimetric analyses of samples (DTA, TG) were performed using a Perkin Elmer TGA-7 thermogravimetric analyzer at a heating rate of 15 °C/min under nitrogen atmosphere, Lyon 2 - France. Microanalyses of elements carbon, hydrogen, nitrogen, sulphur and oxygen; were performed on the automatic Perkin Elmer CHNS/O 2400 analyzer Thermoquest, *C.R.A.P.C*-Alger. Scanning Electron Microscop (SEM) was performed Materials Development Center-Draria-Alger.

3. Results and discussion

3.1. XRD result

The XRD pattern of the sample is shown in Fig. 1. It shows many sharp peaks and quite intense, which characterizes a good crystallinity of material. After comparison of the values of this phase at the data bank EVA, we concluded that these values seem to be new data.

The cell parameters determined starting from a monocrystal by XRD, Kappa CCC were: a =12.948(5) Å b =12.948(5) Å c =18.466(5) Å $\alpha = \beta = 90°$ $\gamma = 120°$.

The VAPO-DAP phase is a new structure with space frame obtained by hydrothermal way. The ultimate analysis by technical spectrometries with 4 circles, the plasma gun and CHN/O, gives us the following chemical result:VAPO-DAP = $[Al_5 P_5 V_{0.25} F_{1.4} O_{26}]^{2-} [H_3N (CH_2)_3 NH_3]^{2+}$.

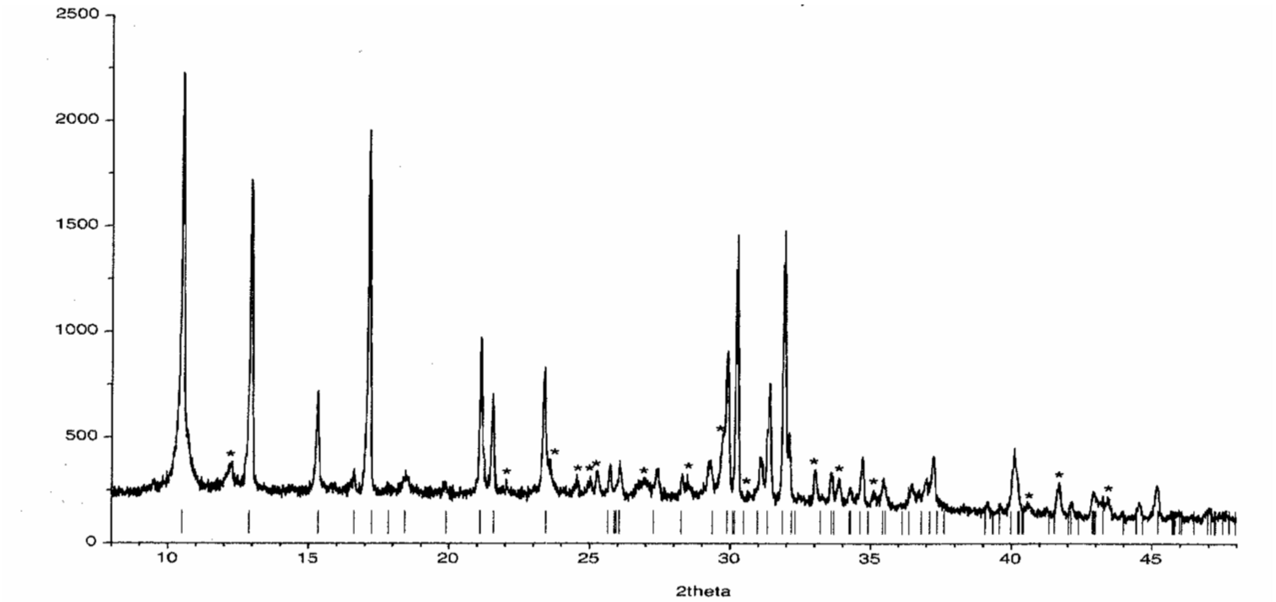

Fig. 1. XRD pattern of product.

Table1. Spectrum analysis of obtained phases

D (A)	9.789	8.891	8.001	6.005	4.890	4.417	4.007	3.795	3.655	3.465	3.333
Intensity	32.9	2.4	100	3.4	20.4	2.9	1.3	5.6	2.5	3.6	6.5
D (A)	3.252	3.167	3.087	2.622	2.524	2.488	2.442	2.360	2.327	2.240	2.138
Intensity	34.6	1.9	6.8	3.1	4.7	0.9	6.9	0.8	1.5	2.0	1.5
D (A)	1.996	1.957	1.834	1.757	1.757	1.676	1.628	1.595	1.544	1.529	
Intensity	3.5	0.8	1.0	2.7	1.6	1.9	1.9	1.3	0.6	0.7	

A crystalline powder results in a fine line spectrum corresponding to the Bragg reflections. Instead, an amorphous substance gives a spread spectrum consists of broad and diffuse ring at small angles and a veil barely modulated high-angle **[14]**. We can note that the material prepared in the presence of hydrofluoric acid recorded a peak of medium intensity at d = 9.789 A ° and another peak trace for d = 2.360 A °. This reaction can be explained by the birth of a new structure in the presence of fluoride ions with a network to 4 D.

3.2. Crystal morphology

The morphology of the synthesized crystals is illustrated by micrographies obtained by SEM, shown in fig. 2. The micrograph below (Fig.2) has noted with satisfaction a light extinction after a 90 ° rotation in polarizing light. The size, shape and extinction confirm the presence of a single crystal. The crystals have parallelepipedic shapes with dimensions varying between10 and 15 μm.

3.3. NMR- MAS ^{31}P, ^{27}Al & ^{51}V spectra

The ^{27}Al NMR spectrum of the synthesized material (Fig.3a) exhibits two peaks: One at -11.3673 ppm and the other one at +39.31 ppm. The first peak, with high intensity is in the range usually observed for octahedral coordination. As for the second one, it is generally reported for tetrahedral coordination. Phosphoric or phosphonic acids react with hydroxyls of the surface of various inorganic oxides such as zirconium oxide or titanium oxide **[18]**.

We had shown that it was also possible to graft alumina by means of phosphonic acids **[19]**. We had shown that it was possible to form hybrid materials by the reaction of phosphonic acids with hydroxyls of alumina. A covalent grafting Al-O-P-C could be obtained **[18-22]**.

The ^{31}P NMR spectrum (Fig.3b) presents a peak of high intensity at – 8.7453 ppm, that may be attributed to the phosphate PO_4^{3-} units **[23, 24].**

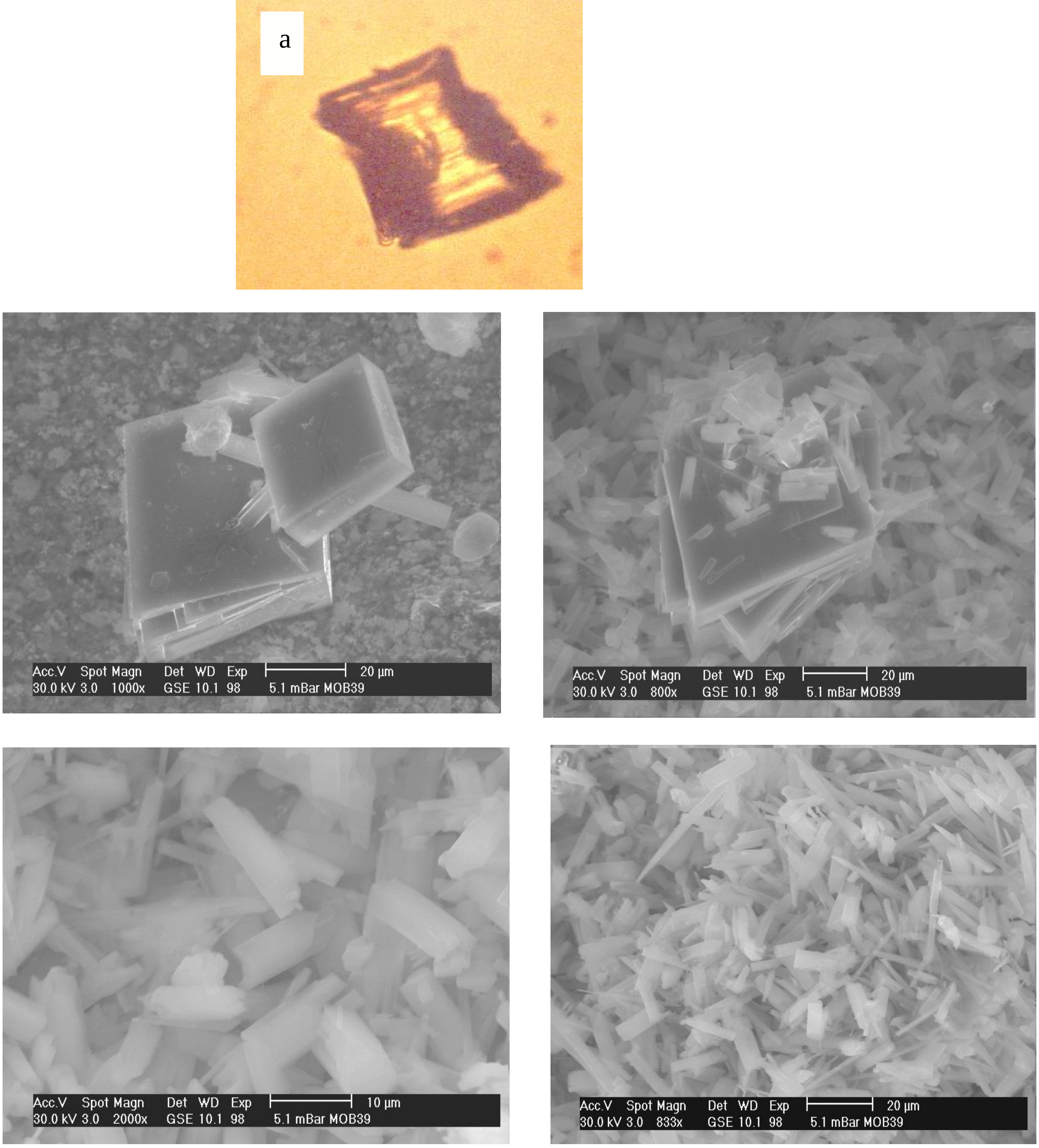

Fig.**2.** S.E.M micrographs of VAPO-DAP. (a) Monocristal

The ^{51}V NMR spectrum (Fig.3c) presents two peaks of high intensity at +3200 ppm and +3400 ppm. Resonance of vanadium in these values indicates two states: the presence of vanadium in a tetrahedral coordination with a environment V-O-Al, ie $V(OAl)_4$ and V-O-P$[V(OP)_4]$. These chemical shifts confirm the presence of the element vanadium in the basic structure of the aluminophosphate and are in good agreement with the results obtained in the literature **[25, 26].**

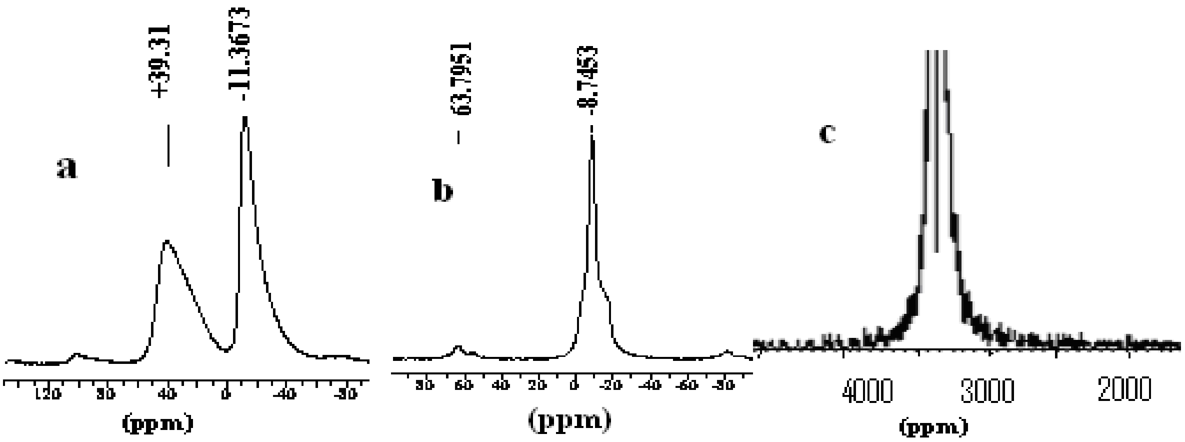

Fig.3. ^{27}Al (**a**), ^{31}P (**b**) & ^{51} V (**c**) NMR-MAS spectra of VAPO-DAP.

3.4 Infra Red Analysis

The FT-IR spectrum (fig.4) was recorded on a Brucker, vector 22 spectrophotometer. It shows vibration bands that could be attributed as follows: 606.46 cm^{-1} (Al-O); 518.40 cm^{-1} (P-O), 1069.20 cm^{-1} (Al-O-P); 1260.91 cm^{-1} (P-O-P). We can note two characteristic vibration bands, one at 1482 cm^{-1} and the other at 1636 cm^{-1} due to the presence of water. Elongation bands can also be noticed at: 3754.25 cm^{-1} (Al-OH); 3639.97 cm^{-1} and 3142.43 cm^{-1} (P-OH-Al) **[28].**

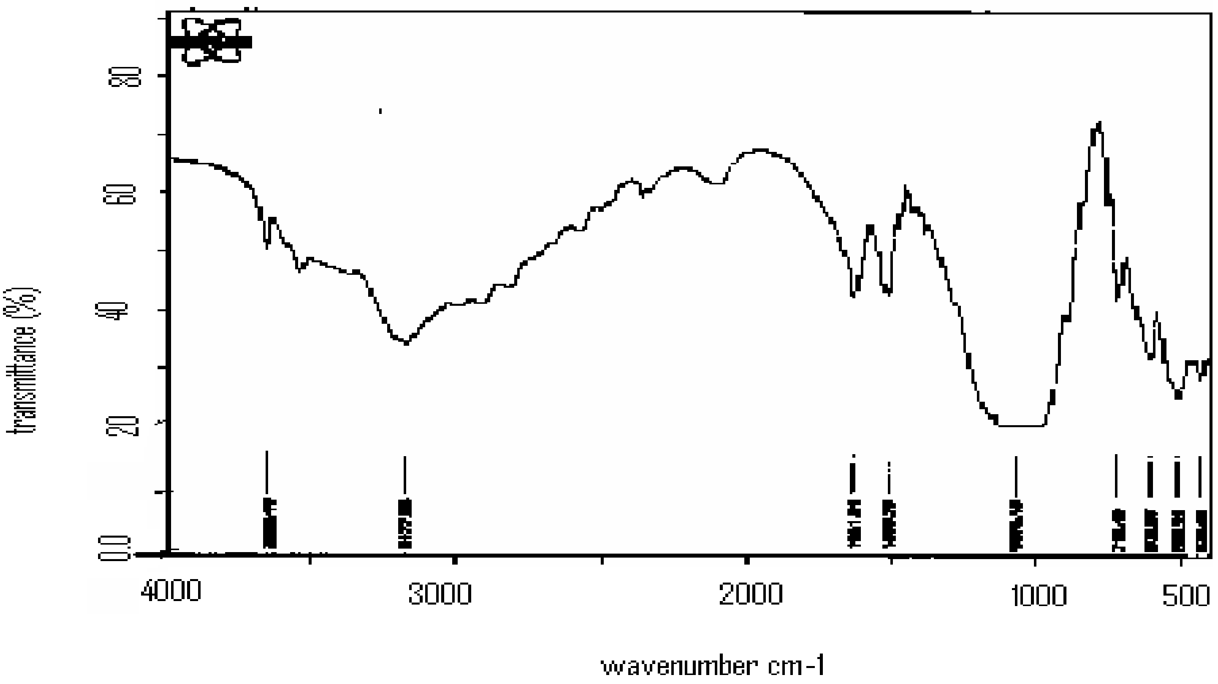

Fig. 4 FT-IR spectrum of VAPO-DAP

3.5. TG analysis of the VAPO-DAP

Figure 5 reports the thermogravimetric curve obtained with a Perkin Elmer TGA-7 thermogravimetric analyzer at a heating rate of 15 °C/min under nitrogen atmosphere.

Two endothermic peaks: one at 50°C and the other more intense to 130°C correspond to dehydration of the material and the amine. The curve shows a weight loss of 30.18 % in the temperature range (400-540°C) that may be attributed to the loss of the organic matter as reported before **[24,25,27].**

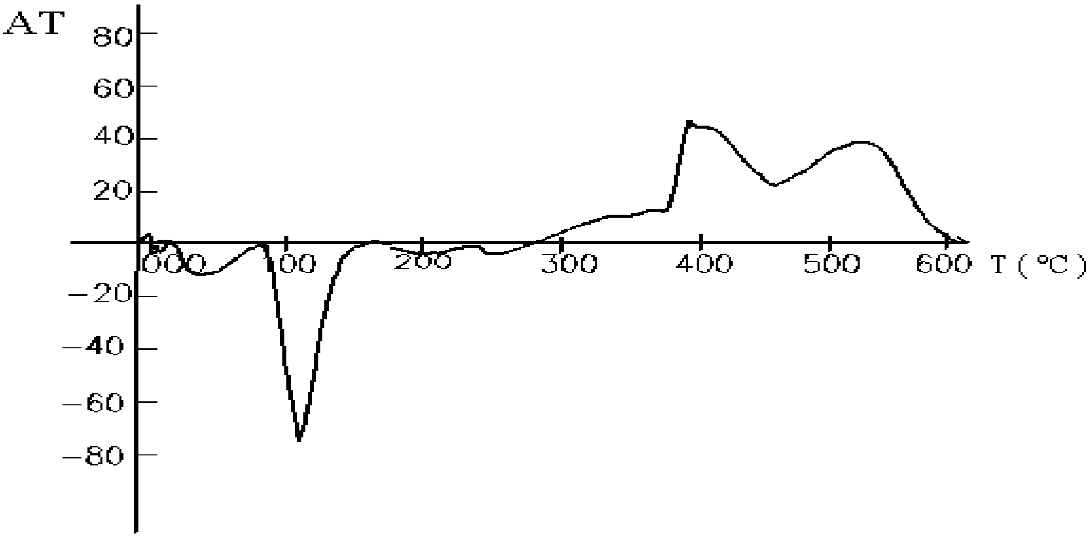

Fig.5. ATD curve of VAPO-DAP

This is confirmed by the elemental analysis of the elements C.H.N./O. The loss of mass is exactly the fraction of the organic template, or nearly a third of the mass of the product. The organic template is responsible for the structural organization in this type of material **[25-32].**

3.6. Chemical analyses

Elemental and ICP analyses were performed respectively with a Perkin Elmer CHN/O analyzer 2400 and a Jobin YVON 32 apparatus. They gave the following values: F (3.23 wt%) P (18.8 wt%) Al (16.4 wt%) V (1.55 wt%) C (4.38 wt%) N (3.40 wt%) H (1.47 wt%) and. These results, added to the thermal analysis and analysis by technical spectrometries with 4 circles give rise to the empirical formula given below.
VAPO-DAP = $[Al_5 P_5 V_{0.25} F_{1.4} O_{26}]^{2-}$ $[H_3N(CH_2)_3NH_3]^{2+}$.

3.7. Cyclohexane oxidation

The study is to oxidize cyclohexane to cyclohexanol as a function of time and temperature in an oxidizing environment. Several tests were performed using an electrochemical cell, volume of 100 ml. The working temperature is 50 ° C, 60 ° C and 70 ° C with times varying between 1, 2, 4, 6 and 8 h. A chromatogram is shown in figure 6.

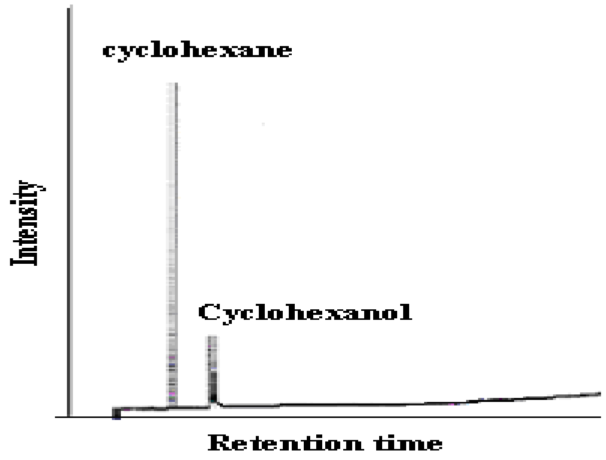

Fig 6. Chromatogram of synthetic products in presence of VAPO-DAP

Table 2 summarizes the results obtained in the presence of the material VAPO-DAP as a function of temperature (50 ° C, 60 ° C and 70 ° C and residence time).

Table 2. Percentages of Cyclohexane and Cyclohexanol function of the temperature for the VAPO-DAP

Temperature (°C)	Yield (%)	Identification
50	82.02	Cyclohexane
	16. 21	Cyclohexanol
60	83.17	Cyclohexane
	16.99	Cyclohexanol
70	78.73	Cyclohexane
	19.91	Cyclohexanol

Conclusion

By the substitution of a part of aluminiumatoms with vanadium and in the presence of D.A.P as organic template, an aluminophosphate was obtained which may have original potential properties.
Our promising important applications in progress on this material is the aerial oxidation of cyclohexane to cyclohexanol, in the growing field of solvent-free industrial reactions, in the important area of clean technology, and like molecular sieve.

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