

Synthesis and characterization of vanadiumoxidecatalysts supported on copper orthophosphates

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Abstract. Synthesis of a pure copper orthophosphate (**CuP**) prepared by Coprecipitation, and **CuP** modified by impregnation of vanadium (2-12 wt % of V₂O₅) have been carried out. The solids obtained were investigated as synthesized or after calcination by various physico-chemical techniques such as X-Ray Diffraction (XRD), Infrared Spectroscopy (IR), Thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The results revealed that the solids **V/CuP** consisted of copper orthophosphate Cu₃(PO₄)₂ as major phases, together with V₂O₅ as minor phase. The diffraction lines of V₂O₅ increase by increasing the vanadium content. **Key word-** Copper orthophosphate **CuP**, Vanadium catalysts supported on copper orthophosphates **V/CuP**, XRD, DTA-TGA.

1.Introduction

Metal phosphates may be classified by their phosphate block units (PO₄³⁻, HPO₄²⁻, H₂PO₄⁺, P₂O₇⁴⁻ and P₄O₁₂⁴⁻) and attract increasing interest for environmental and technological fields [1]. In environmental field, the formation of metal phosphates help remove phosphate from waste waters, while their dissociations help regulate the slow release of fertilizers in acidic soils [2]. In technological field, the interest of metal phosphates is mainly focused on areas such as laser host [3], ceramic [4], electric [5], magnetic [6], fertilizer [7], and catalytic [8] processes because of their valuable physical–chemical properties and reactivity. Consequently, metal phosphates have become a hot research topic in academic (material and chemical sciences) and industrial fields in the recent years [9–11]. Metal phosphate group, is a promising candidate for application in the fields of catalysis, electrics, ion exchange and conductors [12–17]. Because of their acidity and porosity, layered materials represent a vast class of intercalating compounds with useful chemical and thermal properties, which have been extensively used as heterogeneous catalysts [8,18]. Furthermore, The catalysts based on vanadium oxide are used in several industrial processes for production of important chemicals such as sulphuric acid, maleic andphthalic anhydride, and for the reduction of environmental pollution e.g. nitrogenoxides from flue gas of power plants [19-21]. Vanadium oxide catalysts have been tested in a number of heterogeneous catalytic oxidation reactions such as: a) Selective oxidation of alkanes to olefins (oxidative dehydrogenation reaction) [22-24] and to aldehydes and acids [25-27]. b) Selective oxidation of olefins to unsaturated aldehydes and acids, nitriles, dienes, and organic acids [28-30]. The most of vanadia based catalysts consist of a vanadium oxide phase deposited on the surface or in pores of an oxide support. Initially, the support was considered as inert substance that provided a high surface area to carry the active metal oxide component or to improve the mechanical strength of the catalyst material. Deposition of a metal oxide on the surface of another oxide was proposed to improve the catalytic activity of the active metal oxide phase due to a gain in surface area and mechanical



strength[20-25]. However, numerous studies in the last decade indicated that the activity and selectivity of supported metal oxide catalysts are significantly affected by the properties of the support oxide material, and that the dispersed phase has a particular structure and properties different from that of the bulk oxide.

The attempt of this work is to prepare the pure copper orthophosphate **CuP** by coprecipitation, and **CuP** modified by impregnation of vanadium oxide (2-12% of V_2O_5). Additionally, the studied powders were characterized by thermogravimetry–differential thermogravimetry (TG/DTG), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and UV-Visible. The data obtained will be important for further studies of the compound.

2. Experimental

Copper orthophosphate **CuP** were synthesized upon evaporation to dryness from aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $(NH_4)_2HPO_4$. The resulting solids were dried for 12h at 120°C and were finally calcined in air at 450°C for 10h and at 650°C for 10h.

A series of vanadium catalysts V/CuP were prepared using impregnation method, over an CuP support. A mass of metavanadate d'ammonium NH_4VO_3 calculated to yield the desired percentage of vanadium on the support, was dissolved in a predetermined volume of distilled water.

The impregnation catalysts V/CuP were dried at 120°C for 12h and calcined under air flow at 450°C during 10h and at 650°C for 10h.

3. Characterization techniques

The X-ray diffraction (XRD) analysis was performed for the fresh catalyst using Bruker-eco D8 Advance diffract meter with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns were scanned from 5 to 70 θ .

TGA–DTA analysis has been recorded with a TA Instruments balance, model SDT 2966 (TGA–DTA). It allows obtaining simultaneous DTA and TGA diagrams under similar experimental conditions. Experiments were performed under an N_2 flow, from 298 K to 1073 K using a heating rate of 5°C/min.

Diffuse reflectance infrared spectra for the synthesized solids were recorded from 4000 to 400 cm^{-1} on a Nicolet 460 spectrophotometer.

UV–Visible spectra in diffuse reflectance mode were recorded by Shimadzu UV-2400PC Series spectrometer, from 200 to 1000 nm.

4. Results and Discussion

The TG/DTA curves of CuP are shown in Figure 1. The TG curve of CuP shows the three weight loss steps in the range of 50–670°C. The weight loss steps in the TG curve were observed in ranges of 50–150°C and 150–320°C. The corresponding observed weight losses were 4.372% and 41.524% by mass, which correspond to 0.44 mol of water and 4.15 mol of ammonium nitrate and water, respectively. The first stage of the weight loss was related to the loss of moisture because it is not stable over 100°C. While the second stage was due to the loss of water molecules from overlapping reaction the loss of coordination water (dehydration reaction) [31-32]. These two stages appear in the corresponding DTA curve as two endothermic peaks at 130 and 290°C.

The third stage of the weight loss was related to the start of dehydroxylation of libenthite $Cu_2(PO_4)(OH)$ which leads to an orthophosphate $Cu_3(PO_4)_2$, corresponding an one endothermic peaks at 330°C. The endothermic peak appeared at 605°C corresponds to the crystallization of Orthophosphate $Cu_3(PO_4)_2$.

The TGA curve of the solid V(10%)/CuP dried at 110 ° C (Figure 2) has two mass loss between room temperature and 670°C. These weight losses are due to the removal of water and ammonia from the structure metavanadate. The endothermic peak appeared at 605°C corresponds to the crystallization of Orthophosphate $Cu_3(PO_4)_2$. While the other endothermic peak at 645°C can be attributed to

crystallization of the V_2O_5 phase. The formations of $Cu_3(PO_4)_2$ and V_2O_5 oxide will be confirmed by XRD and FTIR.

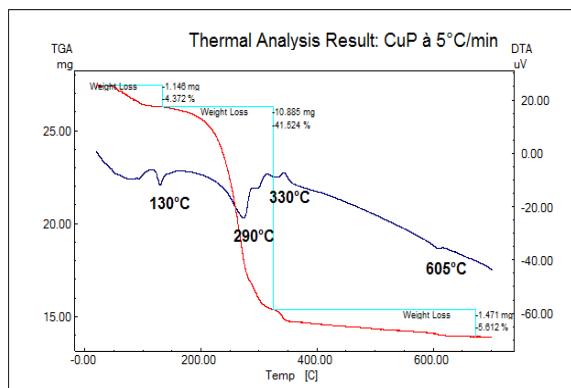


Figure 1. TGA-TDA curves for pure solid CuP

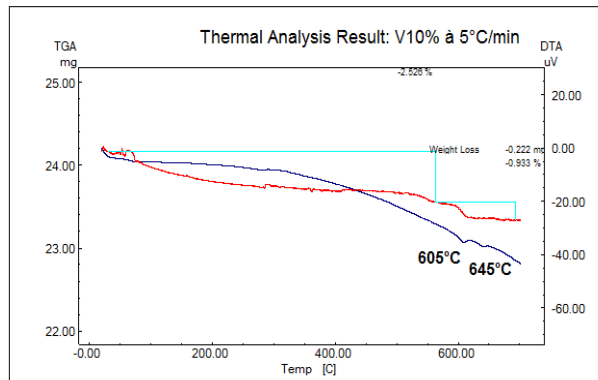


Figure 2. TGA-TDA curves for solid V(12%)/CuP

XRD pattern of the vanadium oxide catalysts supported on copper orthophosphate (V/CuP) calcined at 450°C and 650°C are shown in Figure 3 and figure 4, respectively.

The pure CuP solid treated at 450°C exhibits broad diffraction lines corresponding $Cu_3(PO_4)_2$ (PDF Index Name : Copper Phosphate .ref cod: 01-070-0494), and also some weaker diffraction stripes ($2\theta = 15^\circ$) have been assigned to libethenite $Cu_2(PO_4)(OH)$ (PDF Index Name : Copper Phosphate .ref cod: 01-083-1557). Progressively with the increase in temperature at 650°C (Figure 4), diffraction lines of the copper orthophosphate sharpen indicating a better crystallization of $Cu_3(PO_4)_2$ (PDF Index Name : Copper Phosphate .ref cod: 01-070-0494).

The solids impregnated with vanadium treated at 450°C lead not only to the previous phase identified for $Cu_3(PO_4)_2$ but also to a new crystalline phase V_2O_5 (PDF Index Name : Vanadium Oxide ; ref cod: 01-072-0433). At high temperature treatment (650°C), another structure of vanadium oxide V_2O_5 is clearly identified (PDF Index Name: VanadiumOxide; ref cod: 00-053-0538). This suggests that vanadium oxide is well dispersed over the surface of the copper orthophosphate.

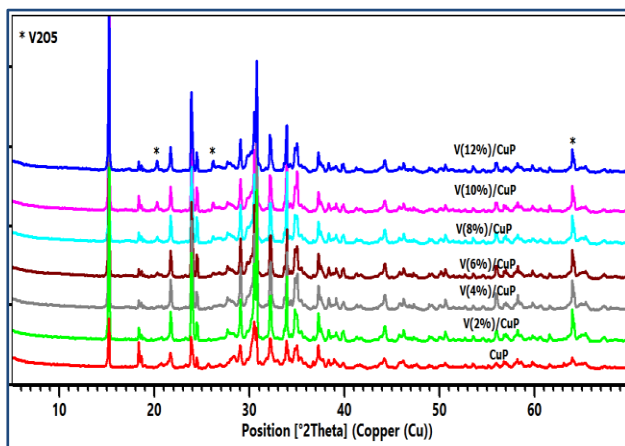


Figure 3. XRD patterns of V/CuP (450°C).

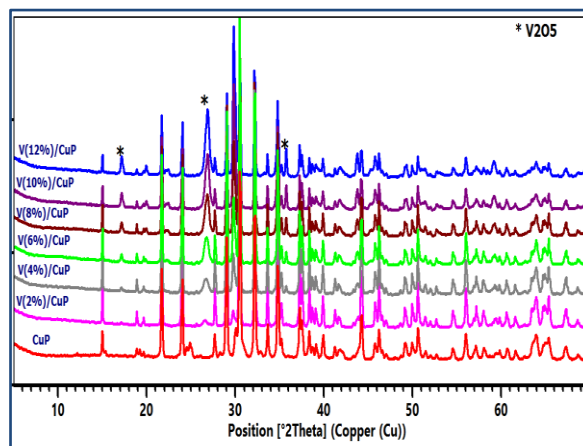


Figure 4. XRD patterns of V/CuP (650°C).

(Vanadium Oxide ; ref cod: 01-072-0433)		(Vanadium Oxide ; ref cod:00-053-0538)	
Crystal system:	Orthorhombic	Crystal system:	Orthorhombic
Space group:	Pmmn	Space group:	P E
Space group number:	59		
a (Å):	11,5100	a (Å):	7,1000
b (Å):	4,3690	b (Å):	6,2940
c (Å):	3,5630	c (Å):	3,5780
Alpha (°):	90,0000	Alpha (°):	90,0000
Beta (°):	90,0000	Beta (°):	90,0000
Gamma (°):	90,0000	Gamma (°):	90,0000

The FTIR spectra of the synthesized V/CuP are shown in Figure 5. For characteristic vibration of CuP calcined at 650°C, FTIR bands are assigned according to the literature [33, 34] based on the fundamental vibrating unit PO_4^{3-} anion. One of the most noteworthy features of the spectrum is the presence of the strong bands at 1120, 965-935, 608-527 and 406 cm^{-1} . These bands can be assigned to the $\nu_{\text{as}}(\text{PO}_4^{3-})$, $\nu_{\text{s}}(\text{PO}_4^{3-})$, $\delta_{\text{s}}(\text{PO}_4^{3-})$ and $\delta_{\text{s}}(\text{PO}_4^{3-})$, respectively. The characteristic bands of groups (PO_4^{3-}) refine, divide, which reflects a structural evolution of crystalline compound.

For FT-IR spectra of V/CuP and comparing with the CuP samples, it is clear that the vibrational bands of vanadate are observed in the regions 800 cm^{-1} , 652 cm^{-1} , 1024 cm^{-1} and 452 cm^{-1} and 459 cm^{-1} ; These bands can be assigned to the $\nu_{\text{as}}(\text{V-O-V})$, $\delta_{\text{as}}(\text{V-O-V})$, to the symmetric stretching V = O bond and the vibration of O-V = O respectively [35-38]. In addition When the V_2O_5 content increased the bands intensity of V/CuP samples increased because the carrier surface was being covered by the active components V_2O_5 oxide.

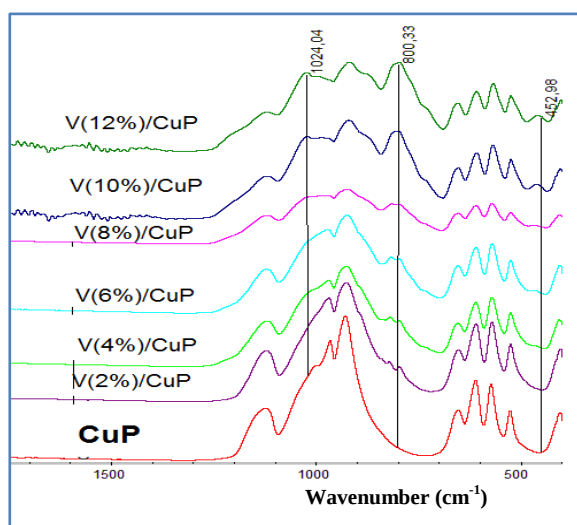


Figure 5. FTIR spectra of V/CuP solids

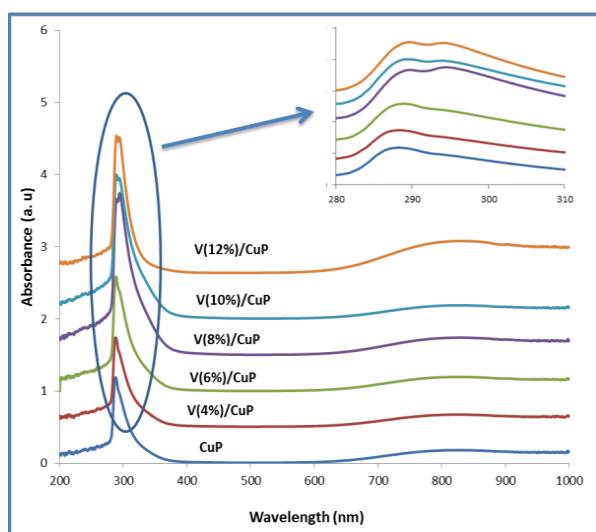


Figure 6. UV-Vis spectra of V/CuP solids.

The UV-Vis spectra of the V/CuP samples are compared in Figure 6. All spectra of V/CuP samples exhibit two major CTLM (charge transfer ligand-metal) bands centered at about 289 and 294 nm of P-O, Cu-O and V-O. In addition, the V/CuP samples exhibit a small and broad visible absorption band with a maximum at 800 nm corresponding to d-d transitions ($d^{10}3d^94s^1 \rightarrow d^{10}3d^94s^0$) of Cu^{2+} . This last Cu^{2+} is the only known ion having the $3d^9$ configuration [39-43]. The energy diagram for d^9 system in octahedral symmetry is just the inverse of that for octahedral d^1 system. It is well known that the spectra of all solids containing copper ion have at least wide and unsymmetrical broad visible band centered near 800 nm [41; 44]. A comparison with the spectra of aqueous and crystalline cupric

complexes shows that the Cu^{2+} ions must be present in approximately octahedral coordination [42; 44; 45]. For the catalysts supported vanadium oxide catalysts, also the strong bands between 200 and 300 nm originating from O^{2-} , V^{5+} charge transfer transitions of low coordinated V^{5+} centers according to previous assignments [46–48].

No appreciable changes of coordination of Cu^{2+} and V^{5+} ions composition are detected from UV–vis spectra. This is in accordance with results obtained from XRD and IR.

5. Conclusions

In this work we have reported the synthesis of a pure copper orthophosphate (CuP) and CuP modified by introduction of vanadium (2–12 wt % of V_2O_5) through an easy, cost- and timesaving route, in comparison with previous synthesis of other metal orthophosphates. The XRD and FTIR results confirmed the formation of $\text{Cu}_3(\text{PO}_4)_2$ product and we have demonstrated also the formation of the V_2O_5 on the surface of support. The solids obtained are necessary for theoretical study, applications development, and catalysis reaction.

In perspective, these catalysts V/CuP will be used for the sulfuric acid production and oxidative dehydrogenation of lower alkanes. The influence of acid–base properties of vanadium catalysts supported on copper orthophosphates in this reaction will be studied by catalytic decomposition of Isopropyl Alcohol.

References

- [1] Averbuch-Pouchot M.T., Durif A., 1996 Topics in Phosphate Chemistry, World Scientific Publishing Co. Pte. Ltd., Singapore,
- [2] Silber A., Bar-Yosef B., Levkovitch I., Kautzky L., Minz D., 2008; Kinetics and mechanism of pH-dependent Mn(II) reactions in plant-growth medium, *Soil Biology and Biochemistry* **40** p2787–2795.
- [3] Jouini A., Gacon J.C., Ferid M., Trabelsi-Ayadi M., 2003; Luminescence and scintillation properties of praseodymium poly and diphosphates, *Optic Materials* **24** p175–180.
- [4] Hsiang H.I., Mei L.T., Lin Y.H., Formation and growth of manganese phosphate passivation layers for NTC ceramics, 2009 *Journal of Alloys Compounds* **48** p723–728.
- [5] Adam L., Guesdon A., Raveau B., Unique charge ordering of manganese in a new mixed valent phosphate $\text{K}_3\text{Mn}_3\text{II MnIII}(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$, 2009; *Journal of Solid State Chemistry* **182** p2338–2343.
- [6] Feng D., Wang C., Cheng W., Li G., Tian S., Liao F., Xiong M., Lin J., 2009 Synthesis, crystal structure, and magnetic properties of $\text{K}_4\text{Mn}_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_2$, *Solid State Sciences*, **11** p845–851.
- [7] Yuan A., Wu L., Bai S., Ma Z., Huang Tong Z., Standard molar enthalpies of formation for ammonium/3d-transition metal phosphates $\text{NH}_4\text{MPO}_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$), 2008; *Journal of Chemistry and Engineering Data* **53** p1066–1070.
- [8] Jibril B.Y., Al-Zahrani S.M., Abasaeed A.E., Propane oxidative dehydrogenation over metal pyrophosphates catalysts, 2001 *Catalysis Letters* **74** p145–148.
- [9] Boonchom B., Baitahe R., Jounmunkong Z., Vittayakorn N., Grass blade-like microparticles $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ prepared by a simple precipitation at room temperature, 2010 *Powder Technology* **203** p310–314.
- [10] Qiu G., Gao Z., Yin H., Feng X., Tan W., Liu F., Synthesis of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ by refluxing process at atmospheric pressure, 2010 *Solid State Sciences* **12** p808–813.
- [11] Ping Ong S., Jain A., Hautier G., Kang B., Ceder G., Thermal stabilities of delithiated olivine MPO_4 ($\text{M} = \text{Fe}, \text{Mn}$) cathodes investigated using first principles calculations, 2010 *Electrochemistry Communications* **12** p427–430.
- [12] Boonchom B., 2009 Kinetic and thermodynamic studies of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ by non-isothermal decomposition data, *Journal of Thermal Analysis and Calorimetry* **98** p863–871.
- [13] Boonchom B., Danvirutai C., 2008 A simple synthesis and thermal decomposition kinetics of $\text{MnHPO}_4 \cdot \text{H}_2\text{O}$ rod-like microparticles obtained by spontaneous precipitation route, *Journal*

- of Optoelectronics and Advance Materials 10 p492–499.
- [14] Brandova D., Trojan M., Arnold M., Paulik F., Paulik J., 1988 Mechanism of the dehydration of $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$, *Journal of Thermal Analysis* 34 p673–678.
 - [15] Brandova D., Trojan M., Arnold M., Paulik F., Paulik J., 1988 Mechanism of the dehydration of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$, *Journal of Thermal Analysis* 34 p1449–1454.
 - [16] Rosa S., Lundager Madsen H.E., 2010 Influence of some foreign metal ions on crystal kinetics of brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, *Journal of Crystal Growth* 45 p2983–2988.
 - [17] Brandova D., Trojan M., Paulik F., Paulik J., 1987 Mechanism of the dehydration of $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$, *Journal of Thermal Analysis* 32 p1923–1928.
 - [18] Aramendi A. M.A., Borau V., Jimenez C., Marinas J.M., Romero F.J., 1999 Synthesis and characterization of magnesium phosphates and their catalytic properties in the conversion of 2-hexanol, *Journal of Colloid Interface Sciences* 217 p288–298.
 - [19] Trifiro F., Grzybowska B., 1997 Vanadia catalysts for selective oxidation of hydrocarbons and their derivatives and references therein special issue of *Appl. Catal. A Gen.* 157.
 - [20] Bond G.C., Tahir S.F., 1991 Influence of phosphorus and potassium additives on the properties of vanadia/titania, catalysts *Catal Today*. V 10, Issue 3, 30 September 1991, P 393–395.
 - [21] Deo G., Wachs I.E., Haber J., 1994; Supported vanadium oxide catalysts: Molecular structural characterization and reactivity properties; *Crit. Rev. Surf. Chem.* 4 p141.
 - [22] Khodakov A., Olthof B., Bell A.T., Iglesia E., 1999; Structure and Catalytic Properties of Supported Vanadium Oxides: Support Effects on Oxidative Dehydrogenation Reactions; *J. Catal.* 181 p205.
 - [23] Chen K., Khodakov A., Yang J., Bell A.T., Iglesia E., 1999; Isotopic tracer and kinetic studies of oxidative dehydrogenation pathways on vanadium oxide catalysts; *J. Catal.* 186 p325.
 - [24] Concepcion P., Lopez Nieto J.M., Perez-Pariente J., 1995; Oxidative dehydrogenation of propane on VAPO^{-5} , $\text{V}_2\text{O}_5/\text{ALPO}_4^{-5}$ and $\text{V}_2\text{O}_5/\text{MgO}$ catalysts. Nature of selective sites; *J. Mol. Catal. A: Chem.* 97 p173.
 - [25] Banares M.A., Alemany L.J., Granados M.L., Faraldos M., Fierro J.L.G., 1997; Partial oxidation of methane to formaldehyde on silica-supported transition metal oxide catalysts; *Catal. Today* 33 p73.
 - [26] Parmaliana A., Fursteri F., Mezzapica A., Scurrell M.S., Giordano N., 1993; *Journal of Catalysis; A Basic Approach to Evaluate Methane Partial Oxidation Catalysts; Volume 143, Issue 1, September 1993, Pages 262-274*
 - [27] Herman R.G., Sun Q., Shi C., Klier K., Wang C.B., Hu H., Wachs I.E., Bhasin M.M., 1997; development of active oxide catalysts for the direct oxidation of methane to formaldehyde; *Catal. Today* 37 p1-14.
 - [28] Vitry D., Morikawa Y., Dubois J.L., Ueda W., (2003); Mo-V-Te-(Nb)-O mixed metal oxides prepared by hydrothermal synthesis for catalytic selective oxidations of propane and propene to acrylic acid; *Appl. Catal. A*, 251 p 411.
 - [29] Stobbe-Kreemers A.W., Seede M., Makkee M., Scholten J.J.F., (1995); heteropolyanions as redox components in heterogeneous wacker oxidation catalysts; *journal of catalysis issue: 2*, V 154, pages: 175 – 186.
 - [30] Lemonidou A.A., 2001; n-Butane Oxidative dehydrogenation Kinetics over Vanadia Magnesia Catalyst; *Appl. Catal. A*, 216 p277.
 - [31] Sadiq M., Bensitel M., Lamonier C., Leglise J., 2008 *Solid State Sciences* 10 p434-437.
 - [32] Boonchom B., Vittayakorn N., 2012; Simple fabrication of polyhedral grain-like microparticle $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{HPO}_4 \cdot \text{H}_2\text{O}$ and porous structure CuZnP_2O_7 ; *Ceramics International*, 38 p411-415.
 - [33] Onmura N., Tagawa T., Goto S., 1998 *Appl. Catal A: Gen* 166 p321.
 - [34] Abadzhieva N., Tzokov P., Uzunow I., Minkov V., Klissurski D., V. Rives; methanol oxidation to formaldehyde on bismuth phosphate-based catalysts; *reaction Kinetics and catalysis letters. issue: 2, volume: 53, year: 1994, pages: 413 - 418*
 - [35] Abello L., Husson E., Repelin Y., Lucazeau G., (1983); Vibrational spectra and valence force

- field of crystalline V_2O_5 ; Spectrochim. Acta 39A p641.
- [36] P.Ettireddy.Reddy and S.Rajender.Varma, 2004; Preparation, characterization, and activity of Al_2O_3 -supported V_2O_5 catalysts; Journal of catalysis catal.221 p93-101.
- [37] Frederickson L.D and Hausen D.M., 1963; Infrared Spectra-Structure Correlation Study of Vanadium-Oxygen Compounds;Anal.Chem.35(7) p818.
- [38] Agunaou M., 1991., Evolution des proprietes physico-chimiques des oxydes $Bi_xGd_{1-x}VO_4$, catalyseurs d'hydrogenation du dioxyde de carbone., thèse de doctorat, Université de Lille,
- [39] Cotton F.A., Wilkinson G., Murrillo C.A., Bochmann M., 1999.Advanced Inorganic Chemistry, 6th ed., John-Wiley-Interscience, New York,
- [40] Bates T., in: J.D. Mackenzie (Ed.)1962;Modern Aspects of the Vitreous State, Butterworths, London 2 p195.
- [41] Bamford C.R., 1977; Color Generation and Control in Glass;Elsevier Science Publisher, Amsterdam,
- [42] Jorgensen C.K., 1957; Recent progress in ligand field theory;Acta Chem. Scand. 11 p73.
- [43] Duran A., Fernandez Navarro J.M., 1985 ; The colouring of glass by Cu^{2+} ions; Phys. Chem. Glasses 26 p126.
- [44] Cable M., XiangZ.D., 1989 ; Cuprous-cupric equilibrium in soda-lime-silica glasses melted in air;Phys. Chem. Glasses 30 p237.
- [45] Morsi M.M., Metwalli E.S., Mohamed A.A., 1999; Modified chemical method for determination of Cu^+ ions in some Cu containing phosphate glasses and effect of composition on the $Cu^{2+}/Cu(tot)$ ratio; Phys. Chem. Glasses 40 p314.
- [46] Wachs I.E., 1996,Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts, Catal. Today 27 p437.
- [47] Busca G., 2002; Differentiation of mono-oxo and polyoxo and of monomeric and polymeric vanadate, molybdate and tungstate species in metal oxide catalysts by IR and Raman spectroscopy; Raman Spectrosc 33 p348.
- [48] Banares M.A., Wachs I.E., 2002; Molecular structures of supported metal oxides catalysts under different environnements;J. Raman Spectrosc. 33 p359.