SYNTHESIS AND CHARACTERIZATION OF NICKEL-MOLYBDENUM CATALYSTS SUPPORTED ON COPPER ORTHOPHOSPHATES

OUCHABI Mbarka1*, BAALALA Mohammed1, ELAISSI Abdelkrim1, BENSITEL Mohammed1,2**.
1 Laboratoire de Catalyse et Corrosion des Matériaux, Université Chouaib Doukkali, Faculté des Sciences d’El Jadida, BP. 20, El Jadida 24000, Morocco.
*Corresponding author: m.ouchabi@yahoo.fr ; **bensitel.m@ucd.ac.ma

Abstract. Synthesis of a pure copper orthophosphate (CuP) prepared by Coprecipitation, and CuP modified by impregnation of NiMo (2-14 wt % of Ni-Mo oxide) 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 NiMo/CuP consisted of copper orthophosphate Cu₃(PO₄)₂ as major phases, together with NiMoO₄ as minor phase. The diffraction lines of NiMoO₄ increase by increasing the nickel-molybdenum content.

Keywords: Copper orthophosphate CuP, nickel-molybdenum catalysts supported on copper orthophosphates NiMo/CuP, XRD, DTA-TGA.

1. Introduction

The numerous investigations of the systems Cu–P–O and Cu–P–O–H have revealed their rich crystal chemistry. Copper can accommodate various coordinations from tetrahedral or square to pyramidal and octahedral. Thirteen different structures of copper phosphates or hydroxyphosphates have been discovered to date [1]. It is well accepted that there is a close relationship between the morphology and their properties of inorganic materials, that is, morphologies determine their properties since the crystal shape dictates the interfacial atomic arrangement of the material [2-7]. Acidic solids derived from metal orthophosphates are widely used to catalyze various reactions occurring at the gas/solid interface. Acid–base properties and redox properties are amongst important types of surface chemical properties of metal orthophosphate catalysts. A number of NiMo catalysts have been tested in a number of heterogenous catalytic oxidation reactions such as: Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo [8]; The Mo₃NiS₄/NaY catalyst showed much higher activity for HDS of benzothiophene than the Mo₃S₄/NaY catalyst [9]; NiMo/Al₂O₃ catalyst containing nano-sized zeolite Y for deep hydrodesulfurization and hydrodenitrogenation of diesel [10]; Recently Sadiq tested the Influence of acid–base properties of cobalt–molybdenum catalysts supported on magnesium orthophosphates in isomerization of 3,3-dimethylbut-1-ene [11].
The most of nickel-molybdenum oxide based catalysts consist of a NiMoO$_4$ phase deposited on the surface or in pores of an oxide support. 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 Nickel-molybdenum. 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

1.1. Sample preparation

Copper orthophosphate CuP were synthesized upon evaporation to dryness from aqueous solutions of Cu(NO$_3$)$_2$.3H$_2$O and (NH$_4$)$_2$HPO$_4$. The resulting solids were dried for 12h at 120°C and were finally calcined in air at 450°C for 10h.

A series of nickel–molybdenum catalysts NiMo/CuP, were prepared using successive impregnation method, over an CuP support. A mass of nickel nitrate [Ni(NO$_3$)$_2$.6H$_2$O] calculated to yield the desired percentage of nickel on the support, was dissolved in a predetermined volume of distilled water. This volume calculation is based on the pore volume of the support. The impregnated catalysts Ni/CuP were dried at 120°C K for 12 h and calcined under air flow at 450°C during 4 h. A second impregnation over Ni/CuP by an aqueous solution of ammonium heptamolybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O]. Finally, the impregnated catalysts are dried at 120°C during 12 h and calcined under air flow at 450°C for 4 h, finally at this solids calcined at 650°C for 10h to clearly identify the phase obtained.

1.2. Characterization techniques

The X-ray diffraction (XRD) analysis was performed for the fresh catalyst using Bruker-eco D8 Advance diffract meter with Cu-Kα radiation (λ = 1.5418 Å). The XRD patterns were scanned from 5 to 70°.

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.

3. Results and discussion

3.1. DTA and TG analyses

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. Correspond respectively to 4.372% of water and 41.524% of ammonium
nitrate and water. 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 libenethite 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 better crystallization of Orthophosphate Cu$_3$(PO$_4$)$_2$ [12-13].

The TGA curve of the solid NiMo(14%)/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 ammonium heptamolybdate. The endothermic peak appeared at 605°C corresponds to the crystallization of Orthophosphate Cu$_3$(PO$_4$)$_2$. While No peak observed after 605°C attributed to crystallization of the NiMoO$_4$ phase. May be the Nickel-Molybdenum oxide is well dispersed on the surface of the copper orthophosphate or the amount of Nickel-Molybdenum oxide is too small.

3.3. XRD results

The XRD pattern of the nickel-molybdenum oxide catalysts supported on copper orthophosphate NiMo/CuP calcined at 450°C and 650°C are presented 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 (2θ = 15°) 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) [12-13].

From figure 4, The solids impregnated with nickel-molybdenum treated at 450°C lead only to the previous phase identified for Cu$_3$(PO$_4$)$_2$. 
At high temperature treatment (650°C), all the catalysts of the series showed lines characteristic for Copper orthophosphate (figure 4) and all crystalline phases of these solids belong to the anorthic system and crystallize in the P-1 (2) spatial group.

The appearance of peaks at \(2\theta = 26^\circ\) and \(33^\circ\) indicates the presence of Nickel Molybdenum oxide \(\text{NiMoO}_4\) (ref cod: 00-045-0142) this phase belong to the monoclinic, spatial group \(\text{C2/m}\) (12). This suggests that if Nickel-molybdenum-containing phases are present, they are small and poorly crystalline. The formations of \(\text{Cu}_3(\text{PO}_4)_2\) and \(\text{NiMoO}_4\) oxide is well confirmed by XRD.

However, Average crystallite size of \(\text{NiMo/CuP}\) calcined at 450°C and 650°C calculated by applying the debye -scherrer’s equation from the high score software and reported in table 2. The compositions of these solids are nanocrystalline with an average crystallite size of up to about 77 nm. The crystallite size of all solids calcined at 650°C remains stable which confirms the better crystallization of catalysts.

**FIGURE 3.** XRD PATTERNS OF \(\text{NiMo/CuP}\) (450°C).

**FIGURE 4.** XRD PATTERNS OF \(\text{NiMo/CuP}\) (650°C).
### Table 2: Average Crystallite Size of NiMo/CuP solids Calculated from XRD Data.

| Catalysts | CuP | NiMo(2%) | NiMo(4%) | NiMo(6%) | NiMo(8%) | NiMo(10%) | NiMo(12%) | NiMo(14%) |
|-----------|-----|----------|----------|----------|----------|-----------|-----------|-----------|
| Crystallite size (nm) (450°C) | 40.1 | 40.12 | 40.12 | 77.03 | 40.88 | 77.03 | 40.12 | 77.03 |
| Crystallite size (nm) (650°C) | 40.8 | 40.86 | 40.86 | 40.86 | 40.86 | 40.86 | 40.86 | 40.86 |

### 3.3. FTIR results

The FTIR spectra of the synthesized NiMo/CuP are shown in Figure 5. For characteristic vibration of CuP calcined at 650°C, FTIR bands are assigned according to the literature [14-15] based on the fundamental vibrating unit $\text{PO}_4^{3-}$ 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 $\nu_{as}(\text{PO}_4^{3-})$, $\nu_s(\text{PO}_4^{3-})$, $\delta_s(\text{PO}_4^{3-})$ and $\delta_s(\text{POP})$, respectively. The characteristic bands of groups ($\text{PO}_4^{3-}$) refine, divide, which reflects a structural evolution of crystalline compound.

For FT-IR spectra of NiMo/CuP (figure 5) and comparing with the CuP samples, the appearance of the bands at 738, 820 and 870 cm$^{-1}$ indicates the presence of weakly crystallized NiMoO$_4$. From literature the spectrum of molybdate is characterized by appearance the three strong absorption bands at 566, 762 and 848 cm$^{-1}$. The first two are assigned to Mo-0 stretching vibrations with Mo in octahedral coordination. The band at 848 cm$^{-1}$ indicates that part of the Mo is in a tetredral environment [16]. In our case, the broad band centered around 738 cm$^{-1}$ assigned to Mo-0 stretching vibrations with Mo in octahedral coordination. The band at 566 (due to Mo-0 octahedral vibration) is absent, perhaps they may be masked by the bands characteristic of phosphates.

![FIGURE 5. FTIR SPECTRA OF NiMo/CuP SOLIDS](image)
3.4. UV-Visible results

The UV–Vis spectra of the NiMo/CuP samples are compared in Figure 6. All spectra of NiMo/CuP samples exhibit two major CTLM (charge transfer ligand-metal) bands centered at about 289 and 294 nm of P–O and Cu–O. In addition, the NiMo/CuP samples exhibit a small and broad visible absorption band with a maximum at 800 nm corresponding to d–d transitions (d^{10} 3d^{4}s^1) of Cu^{2+}, this results suggested that the Cu^{2+} ions must be present in approximately octahedral coordination [17-18].

For NiMo/CuP samples a broad band between 700 and 800 nm is also probably attributed to reduced Mo ions Mo^{5+} and/or Mo^{4+}. M.C. Abello et al. observed for MoO_3 / Al_2O_3 catalysts two absorption bands at 220 and 260 nm and a broad band in the 280–350 nm region, suggesting that Mo^{6+} octahedral species are mainly present [19-22]. For NiMo/CuP the band around 300 nm probably attributed to Mo^{6+} was observed.

The Ni^{2+} ions, in NiMo/CuP sample (Figure 6), were located in oxygen octahedra. According to the literature data a band around 740 nm indicates the appearance of Ni^{2+} ions in octahedral coordination. Several papers describe the nickel catalysts supported on niobia, titania, magnesia and alumina which were characterized by UV-VIS spectroscopy. The appearance of a band around 660-670 nm noticed for NiO/TiO_2 [23] and NiO/MgO [24] catalysts was attributed to the dispersed octahedrally coordinated Ni^{2+} surface species. Similar results were obtained by Y. Chen et al. (~665 nm) [25] and M.A. Zanjanchi (~660 and 730 nm) [19]. For NiO/Nb_2O_5 well defined bands attributed to octahedrally coordinated Ni^{2+} were observed at ca. 840 nm [26].

![FIGURE 6. UV–VIS SPECTRA OF NiMo/CuP SOLIDS.](image)

4. Conclusions

The In this work we have reported the synthesis of a pure copper orthophosphate (CuP) and CuP modified by introduction of nickel-molybdenum through an easy route, in comparison with previous synthesis of other metal orthophosphates. The XRD and FTIR results confirmed the formation of Cu_3(PO_4)_2 product and we have demonstrated also the formation of the NiMoO_4 on the surface of support. The solids obtained are necessary for theoretical study, applications development, and catalysis reaction.
In perspective, these catalysts NiMo/CuP will be used for hydrodesulfuration reaction. The Influence of acid–base properties of nickel-molybdenum catalysts supported on copper orthophosphates in this reaction will be studied by Catalytic decomposition of isopropanol.

REFERENCES
[1] Baies R., Caignaert V., Pralong V., Raveau B., Inorg. Chem. 44 (2005) 2376–2380.
[2] Chen S., Yu S., Jiang J., Li F., Liu Y., Chem. Mater. 18 (2006) 115–122.
[3] Pan C., Gu Z., Dong L., Acta Chim. Sinica 17 (2009) 1981–1986.
[4] Akla A., Howari H., J. Phys. Chem. Solids 70 (2009) 1337–1343.
[5] Khalavka Y., Sonnichsen C., Adv. Mater. 20 (2008) 588–591.
[6] Xu J., Xue D., J. Phys. Chem. Solids 67 (2006) 1427–1431.
[7] Huang X., Guo C., Zuo J., Zheng N., Stucky G.D., Small 5 (2009) 361–365.
[8] David Kubíčkaa, b, Luděk Kalužab Applied Catalysis A: General Volume 372, Issue 2, 15 January 2010, Pages 199–208.
[9] Mitsugu Taniguchia, Daichi Imamura, Hiromi Ishigea, Youichi Ishiib, Takashi Muratab, Masanobu Hidaib, Takashi Tatsumia1, Hydrodesulfurization of Benzothiophene over Zeolite-Supported Catalysts Prepared from Mo and Mo–Ni Sulfide Clusters, Journal of Catalysis 187(1):139-150 • October 1999.
[10] Hailiang Yin*, Tongna Zhou, Yunqi Liu, Yongming Chai, Chenguang Liu•NiMo/Al2O3 catalyst containing nano-sized zeolite Y for deep hydrodesulfurization and hydrodenitrogenation of diesel Journal of Natural Gas Chemistry 20(2011)441–448
[11] M. Sadiq a, A. Sahibed-dine a, M. Baalala a, K. Nohair a, M. Abdennouri a, M. Bensitel a,*, C. Lamonier b, J. Leglise c Arabian Journal of Chemistry (2011) 4, 449–457
[12] M. Ouchabi, M. Baalala, A. Elaissi, M. Bensitel, J. Mater. Environ. Sci. 7 (4) (2016) 1417-1424.
[13] M. Ouchabi, M. Baalala, A. Elaissi, M. Bensitel, 2017, IOP Conf. Ser.: Mater. Sci. Eng. 186 012013.
[14] Colthup N.B., Daly L.H., Wiberley S.E., Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.
[15] Steger E., Kaßner B., Die infrarotspektren von wasser freien schwer metall-Diphosphaten, Spectrochimica Acta, 24A (1968) 447–456.
[16] Anagha A. Belhekar, Subbiah Ayyappan & Arumugamangalam V. Ramaswamy., J. Chem. Tech. Biotechnol. 1994, 59, 395-402
[17] Morsi M.M., Metwalli E.S., Mohamed A.A., 1999 Phys. Chem. Glasses 40 p314.
[18] Y. Ywasawa, M. Yamagishi, J. Catal., 82, (1983), 373.
[19] H. Aritani, T. Tanaka, T. Funabiki, S. Yoshida, K. Eda and N. Sotani, M. Kudo, S. Hasegawa, J. Phys. Chem., 100, (1996), 19495.
[20] M.C. Abello,, M.F. Gomez, M. Casella, O.A. Ferretti, M.A. Bañares, J.L.G. Fierro, Appl. Cat. A: Gen., 251, (2003) 435.
[21] M.C. Abello, M.F. Gomez, O. Ferretti, Appl. Catal. A: Gen. 207 (2001) 421.
[22] B. Xu, L. Dong, Y. Fan, Y. Chen, J. Catal., 193, (2000), 88.
[23] J.D. Dunitz, L.E.Orgel, J. Phys. Chem. Solids, 3, (1957), 318
[24] J. Wang, L. Dong, Y. Hu, G. Zheng, Z. Hu, Y. Chen, J. Solid State Chem. 157, (2001), 274.
[25] M.A. Zanjanchi, L. Abdollahi, J. Inclus. Phen. Macrocycl. Chem., 39 (1-2), (2001), 151.
[26] N. Rajic, I. Arcon, V. Kaucic, A. Kodre, Croatica Chemica Acta, 72 (2-3), (1999) 645