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Bulletin of Chemical Reaction Engineering & Catalysis, 14 (2) 2019, 283-293

Research Article

Preparation, Characterization, and Catalytic Activity of Tin (Antimony) Substituted and Lacunar Dawson Phosphotungstomolybdates for Synthesis of Adipic Acid

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Received: 6th July 2018; Revised: 21st November 2018; Accepted: 4th December 2018;
Available online: 30th April 2019; Published regularly: 1st August 2019

Abstract

Tin (antimony) substituted and lacunar Dawson phosphotungstomolybdates (α -K₁₀P₂W₁₂Mo₅O₆₁, α -K₈P₂W₁₂Mo₅SnO₆₁ and α -Cs₄SnP₂W₁₂Mo₆O₆₂, and α -Cs₃SbP₂W₁₂Mo₆O₆₂) were synthesized and characterized by Fourier Transform Infra Red (FTIR), nuclear magnetic resonance (³¹P NMR), Visible Ultra Violet (UV-Vis) spectroscopy, and X-ray diffraction (XRD). Their catalytic properties were examined in the oxidation reaction of cyclohexanone at 90 °C and that of cyclohexene at 70 °C to adipic acid (AA), in presence of hydrogen peroxide and in free solvent. The effects of catalyst/substrate molar ratios, hydrogen peroxide flow rate, heteropolysalt composition, and cyclohexanol addition on AA yields were studied. The Cs₄SnP₂W₁₂Mo₆O₆₂ (the most efficient) led to 61 % of AA yield from the cyclohexanone oxidation using a catalyst/substrate molar ratio of 13.3×10⁻⁴, H₂O₂ flow rate of 0.5 mL/h, and a reaction time of 20 h. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Dawson; polyoxometalate; adipic acid; cyclohexanone; cyclohexene

How to Cite: Guerroudj, M.R., Dermeche, L., Mouheb, L., Mazari, T., Benadji, S., Rabia, C. (2019). Preparation, Characterization, and Catalytic Activity of Tin (Antimony) Substituted and Lacunar Dawson Phosphotungstomolybdates for Synthesis of Adipic Acid. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14 (2): 283-293 (doi:10.9767/bcrec.14.2.2905.283-293)

Permalink/DOI: <https://doi.org/10.9767/bcrec.14.2.2905.283-293>

1. Introduction

Polyoxometalates (POMs) are metal-oxide clusters, with great diversity in framework. The most studied in field catalysis, are the Keggin-type followed by Dawson-type POMs [1-8]. These latter, although their synthesis is difficult, present many advantages as a more num-

ber of transition metal atoms (18 against 12 by polyanion) giving thus a more great choice in the polyanion composition variation and therefore in the modification of their acid and oxidative properties. Dawson-type POMs were shown to be effective in various oxidation processes as methanol oxidation [8], 3,4-dihydropyrimidinones synthesis [9], epoxidation of cyclooctene and that of cyclohexene [10], phenol hydroxylation [7], isobutane oxidehydrogenation

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to isobutene [5], adipic acid synthesis [11,12] and other catalytic applications [13]. In this work, we were interested in the Dawson-type POMs application as catalysts, in the cyclohexanone oxidation to adipic acid (AA), important product principally used in nylon synthesis. In industrial process, AA is commonly prepared by oxidation of a mixture of cyclohexanone and cyclohexanol (known as KA oil) using nitric acid in presence of Cu/V catalyst [14-16]. KA-oil was obtained from cyclohexane oxidation in the presence of air. However, the reduction of HNO_3 generates a large amount of greenhouse gases. Among them, N_2O is the most dangerous [17]. An alternative to this process was already the subject of several works.

The used oxidants are molecular oxygen, air, and particularly hydrogen peroxide [18-25]. This latter is easier to handle and in addition, its reduction leads only to the water formation. The AA synthesis using the hydrogen peroxide was examined with different catalysts based on Ni, Co, Mn, Mo, and W [12,18-26]. In recent works, we have shown that the introduction of elements, such as: tin and antimony, into Keggin-type POMs improves the catalytic performance of the solid. The AA yields of ca. 60% were achieved with $\text{NH}_4\text{SnPMo}_{12}\text{O}_{40}$ [22]. On the other hand, we have also demonstrated the efficiency of Dawson-type POMs of composition $\text{K}_6\text{P}_2\text{Mo}_x\text{W}_{18-x}\text{O}_{62}$ ($x = 5,6$) in AA synthesis [12]. So, the objective of this work is to introduce tin

and antimony into this type of material. Dawson-type POMs examined in the AA synthesis have formula of $\alpha\text{-K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, $\alpha\text{-K}_6\text{P}_2\text{Mo}_6\text{W}_{12}\text{O}_{62}$, $\alpha\text{-H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$, $\alpha\text{-K}_{10}\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}$, $\alpha\text{-K}_8\text{P}_2\text{W}_{12}\text{Mo}_5\text{SnO}_{61}$, $\alpha\text{-Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$, and $\alpha\text{-Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$. The AA synthesis was carried out from liquid-phase oxidation of cyclohexanone and/or cyclohexanol and cyclohexene in the presence of hydrogen peroxide (30 %) without solvent, acidic additives, and phase transfer agents. The method is based on that proposed by Nomiya *et al.* [28]. POMs were characterized by FT-IR, ^{31}P NMR, UV-Vis spectroscopy, and XRD.

2. Materials and Method

2.1 POM Synthesis

The $\alpha\text{-K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, 1,4,9,10,15,16- $\text{K}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$, 1,4,9,10,15,16- $\text{H}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$, 1,9,10,15,16-4- $\text{K}_{10}\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}$, and 1,9,10,15,16-4- $\text{K}_8\text{P}_2\text{W}_{12}\text{Mo}_5\text{SnO}_{61}$ (noted $\alpha\text{-P}_2\text{W}_{18}$, $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$, $\alpha\text{-H}_6\text{P}_2\text{W}_{12}\text{Mo}_6$, $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}$, and $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$) were synthesized according to established procedures [28-33]. The $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ and $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}$ were obtained from hexavacant anion $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ according to the method described by Contant [30] and Randall [34]. Figure 1 illustrates successive steps involved in synthesis of W/Mo and W/Mo/Sn Dawson mixed heteropolyanions and Dawson polyhe-

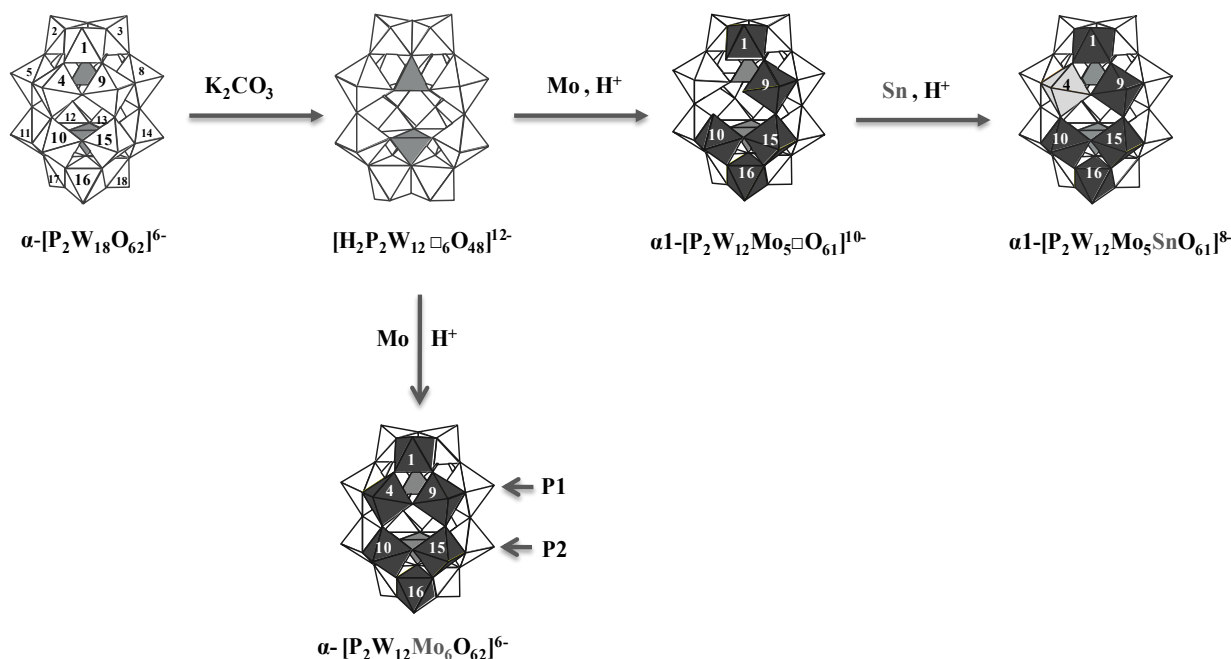
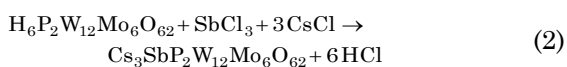
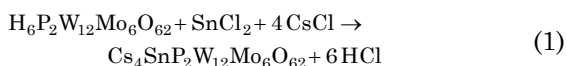


Figure 1. Successive steps of W/Mo and W/Mo/Sn mixed Dawson heteropolyanion, notation, and Dawson polyhedral representation with a numbering of the metallic atoms according to IUPAC recommendations

dral representation with a numbering of the metallic atoms according to IUPAC recommendations. In Dawson heteropolyanion, two types of clusters are present: two terminal trimetallic groups M_3O_{13} (numbers 1-3 and 16-18) and six bimetallic groups M_2O_{10} (numbers 4 to 15) arranged in a double crown [12,28].

The mixed cesium salts, $Cs_4SnP_2W_{12}Mo_6O_{62}$ and $Cs_3SbP_2W_{12}Mo_6O_{62}$, were prepared by precipitation from $\alpha\text{-H}_6P_2W_{12}Mo_6$, $SnCl_2$ or $SbCl_3$, and $CsCl$ according with the stoichiometric ratios (Equations (1) and (2)). $Cs_4SnP_2W_{12}Mo_6$ is dark blue and the $Cs_3SbP_2W_{12}Mo_6$ is green.



2.2 Characterization

Infrared spectra were recorded on the 4000-400 cm^{-1} range on Bruker IFS 66 FT-IR spectrometer using samples prepared as KBr disks. ^{31}P MAS NMR spectra were measured at room temperature on Bruker Avance 400 spectrometer. The 85 % H_3PO_4 was used as an external reference. UV-Vis Diffuse Reflectance spectra were recorded in the 800-200 nm region on Specord 210 Plus Analytic Jena spectrometer equipped with a polytetrafluoroethylene (PTFE) integration sphere. PTFE was used as a reference. X-ray Diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a $Cu\text{-}K\alpha$ ($k = 1.54178 \text{ \AA}$) radiation, in the range of $2\theta = 5\text{-}60^\circ$ at a rate of $0.02^\circ \cdot s^{-1}$.

2.3 Catalytic Methods

The synthesis method is based on that described in the literature [27]. The liquid-phase oxidation was carried out at $90^\circ C$ in the case of cyclohexanone (-one) and at $70^\circ C$ in the case of cyclohexene (-ene), using a 100 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The whole is stirred at 1000 rpm for 20 h reaction time. The reaction mixture is constituted by a calculated amount of POM catalyst and substrate. Hydrogen peroxide (30 %) is added drop wise whenever the POM is reduced. The state of the latter is visualized by the presence of a blue color corresponding to Mo(V) atoms. After adding of H_2O_2 , the catalyst shows a color change from blue to yellow, color characteristic of Mo(VI). It should be pointed out that only two Mo(VI) per Keggin anion can undergo a reduction at a

time and the resultant homogeneous mixture was cooled at $0^\circ C$ overnight. The AA, one of oxidation products, was isolated as white crystals and identified by FT-IR and $^1H\text{-NMR}$ spectroscopy and melting point ($\sim 151^\circ C$). The AA yield is given by the following relationship: AA yield (%) = AA recovered mass \times 100 / theoretical AA mass.

3. Results and Discussion

3.1 Catalysts Characterization

Figure 2 shows FT-IR spectra of the Dawson potassium salts ($\alpha\text{-}P_2W_{18}$, $\alpha\text{-}P_2W_{12}Mo_6$, $\alpha 1\text{-}P_2W_{12}Mo_5\square$ and $\alpha 1\text{-}P_2W_{12}Mo_5Sn$), heteropolyacid $\alpha\text{-}H_6P_2W_{12}Mo_6$ and cesium salts ($Cs_4SnP_2W_{12}Mo_6$ and $Cs_3SbP_2W_{12}Mo_6$). Dawson anion characteristic vibration bands were observed in the low wave number region (500-100

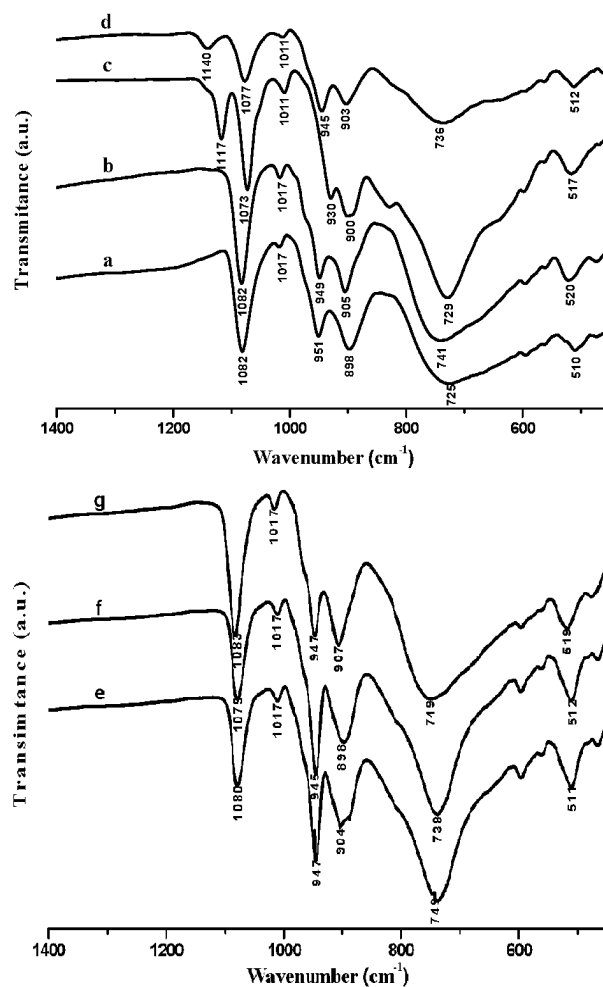


Figure 2. FT-IR spectra of $\alpha\text{-}P_2W_{18}$ (a), $\alpha\text{-}P_2W_{12}Mo_6$ (b), $\alpha 1\text{-}P_2W_{12}Mo_5\square$ (c), $\alpha 1\text{-}P_2W_{12}Mo_5Sn$ (d), $\alpha\text{-}H_6P_2W_{12}Mo_6$ (e), $Cs_4SnP_2W_{12}Mo_6$ (f), and $Cs_3SbP_2W_{12}Mo_6$ (g)

cm⁻¹). The metal-oxygen vibration bands corresponding to inter group M–O_b–M and the intra-group M–O_c–M appear at 898-907 cm⁻¹ and 725-749 cm⁻¹, respectively. The elongation of M=O_d band appear at 930-951 cm⁻¹ range. In the Dawson anion, the phosphorus-oxygen vibration band is very sensitive to its environment. An intense vibration band appears around 1073-1083 cm⁻¹ assigned to the junction phosphorus-bimetallic group M₂O₁₀ (noted (P–Oa)_b) and another around 1011-1017 cm⁻¹ of low intensity attributed to the junction phosphorus-

trimetallic group M₃O₁₃ (noted (P–Oa)_i). FT-IR band observed around 510-520 cm⁻¹ is attributed to δ(P–O) vibration. These results are in agreement with those of the literature [32,33,35]. In addition, in the cases of α1-P₂W₁₂Mo₅□ and α1-P₂W₁₂Mo₅Sn, vibration bands were observed at 1117 and 1140 cm⁻¹, respectively, resulting of the local symmetry decrease attributed to the vacancy presence and to the Sn atom introduction in this vacancy situated in bimetallic group (number 4 as seen in Figure 1).

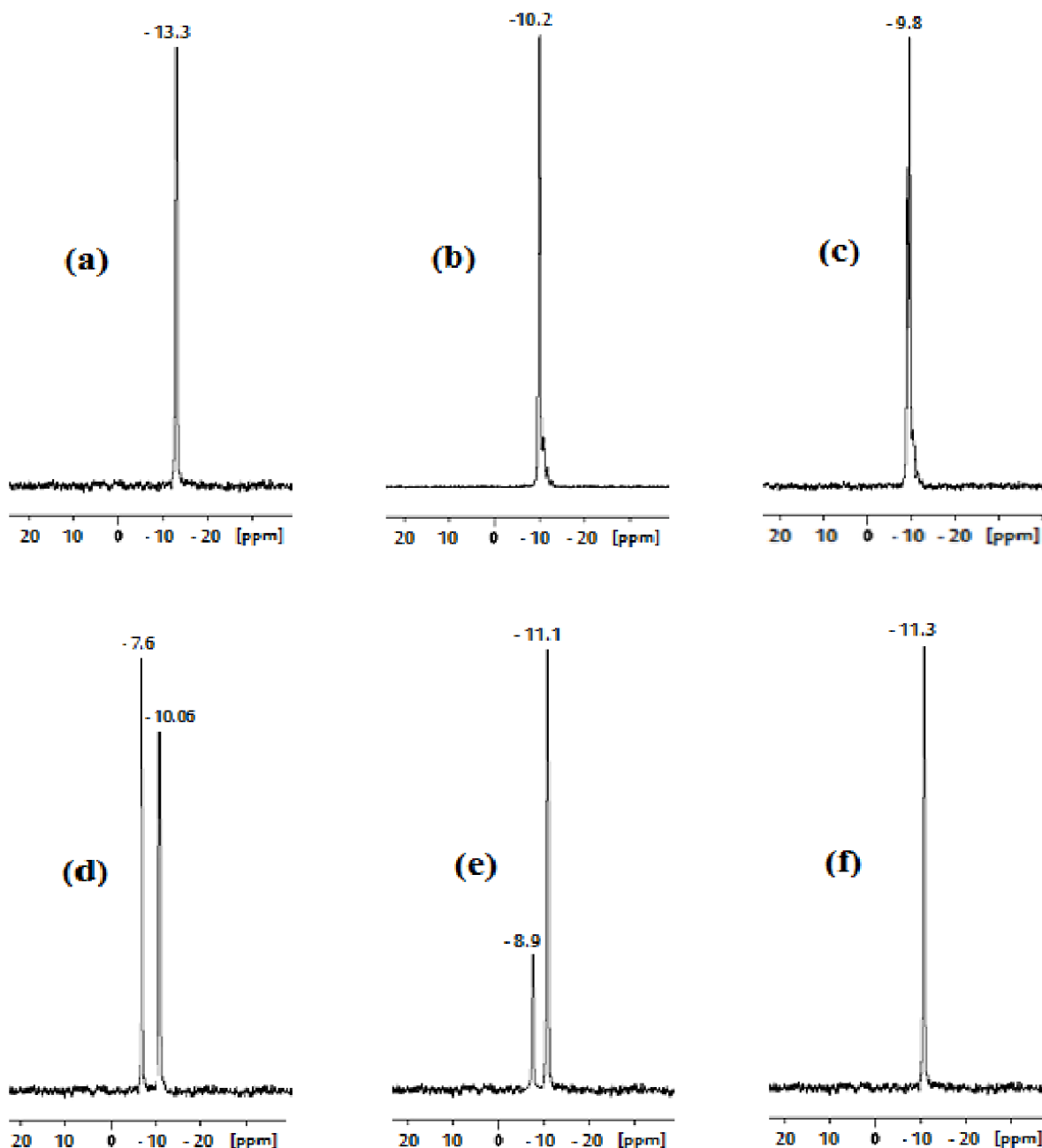


Figure 3. ³¹P NMR spectrum of α-P₂W₁₈ (a), α-P₂W₁₂Mo₆ (b), α-H₆P₂W₁₂Mo₆ (c), α1-P₂W₁₂Mo₅□ (d), α1-P₂W₁₂Mo₅Sn (e) and Cs₄SnP₂W₁₂Mo₆ (f)

The ^{31}P NMR chemical shifts data of the Dawson POMs are presented in Figure 3. Only single resonance peak recorded at -9.8 , -13.3 , -10.2 and -11.3 ppm was observed for $\alpha\text{-H}_6\text{P}_2\text{W}_{12}\text{Mo}_6$, $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}$, $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$, and $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$, respectively, showing that the two half-anions of the Dawson structure are identical. Therefore, these results evidenced the purity of prepared Dawson POMs. The presence of the vacancy in $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\Box$ and the Sn atom insertion in the case of $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$, were highlighted by the two signals observed at -7.6 and -10.06 ppm as well as -8.9 and -11.1 ppm, respectively, results according with those observed in FT-IR spectroscopy. For $\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$, no signal observed, lied probably to the antimony element paramagnetic.

The UV-Vis spectra of $\alpha\text{-P}_2\text{W}_{18}$ (a), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ (b), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\Box$ (c), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$ (d), $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ (e), and $\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$ (f) (Figure 4) show a large band

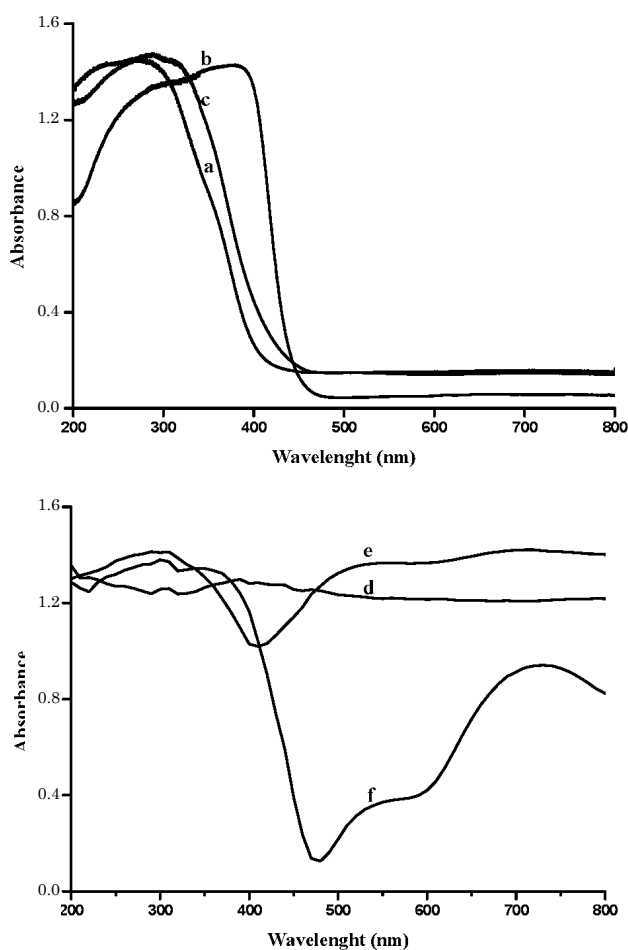


Figure 4. UV-vis/diffuse spectra of $\alpha\text{-P}_2\text{W}_{18}$ (a), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ (b), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\Box$ (c), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$ (d), $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ (e), and $\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$ (f)

in 200-500 nm wavelengths domain assigned to oxygen-metal charge transfer (LMCT), corresponding to the oxidation state VI of metal [8,36-41]. In the case of substituted POMs, the introduction of tin and antimony led to the appearance to another LMCT band above 700 nm that can attributed to molybdenum atoms in an oxidation state V. This observation was already reported in the case of substituted Keggin-type POMs [37-42]. The intensity of this band increases following the sequence $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6 > \alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn} > \text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$. It was also reported that the Mo(VI) reduced amount increases with the band intensity [37,38]. These observations suggest a partial reduction of POMs confirmed by the observed blue color during their preparation. This suggests that an electron exchange takes place between Sn(II) or Sb(III) and Mo(VI) (Equations (3) and (4)).

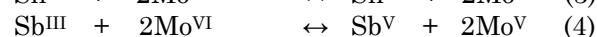
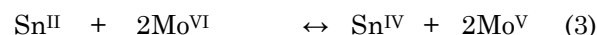


Figure 5 shows the X-ray patterns of prepared salts. The XR pattern of $\text{K}_6\text{P}_2\text{W}_{18}$ is characteristic of a triclinic system, with the following parameters: $a = 12.8600 \text{ \AA}$, $b = 14.8300 \text{ \AA}$, $c = 22.3400 \text{ \AA}$, $\alpha = 94.400^\circ$, $\beta = 116.870^\circ$ and $\gamma = 115.600^\circ$ and spacial group $P\bar{1}$ (2), according to the literature data [43-45]. The $\alpha\text{-K}_6\text{P}_2\text{W}_{12}\text{Mo}_6\text{O}_{62}$ (Figure 5b) presents also X-ray pattern characteristic of a triclinic system. X-ray diffraction patterns of $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$ (Figure 5 d) and $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ (Figure 5e) are similar and appear to crystallize in a different system from the triclinic system. It is the same for $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\Box$ (Figure 5c) and

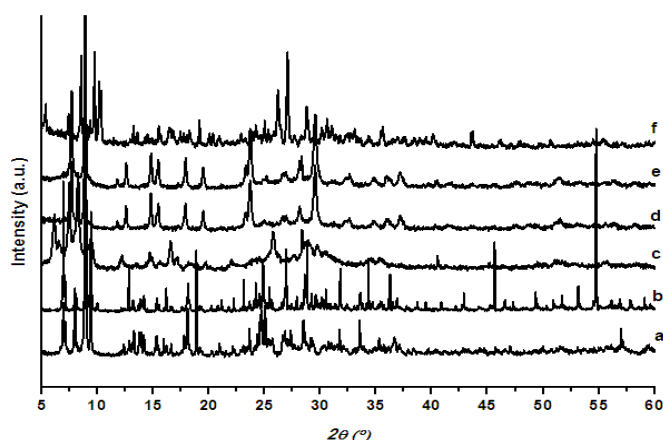


Figure 5. XRD patterns of $\alpha\text{-P}_2\text{W}_{18}$ (a), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ (b), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\Box$ (c), $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$ (d), $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ (e), and $\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$ (f)

$\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$ (Figure 5f) salts that present totally different X-ray patterns which would suggest that these two salts would also crystallize in different unidentified systems in the frame of this work. These results evidenced the influence of the composition of the POM on its crystalline structure.

3.2 Catalytic Tests

The catalytic performance of $\alpha\text{-H}_6\text{P}_2\text{W}_{12}\text{Mo}_6$, $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$, $\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{□}$, $\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$, $\alpha\text{-Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ and $\alpha\text{-Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$ Dawson type salts were examined in adipic acid synthesis from oxidation of both cyclohexanone at 90 °C and cyclohexene at 70 °C, in the presence of hydrogen peroxide (30 %) and free solvent. It was showed that the substrate oxidation to AA did not take place in absence of catalyst and when the reaction was carried out in one pot (substrate + catalyst + hydrogen peroxide) [12, 20-22].

Catalytic tests were repeated three times in the case of cyclohexanone oxidation and twice

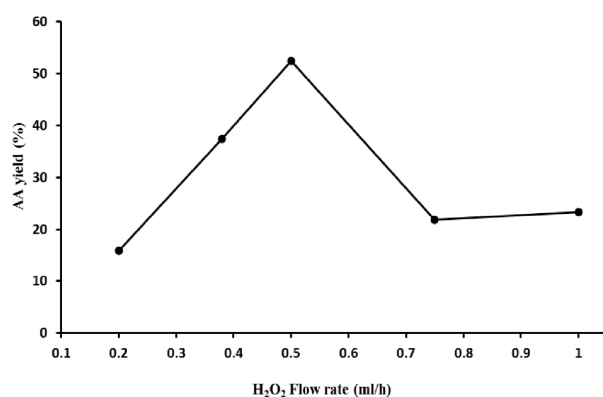


Figure 6. Adipic acid yields as function of hydrogen peroxide flow rate. Reaction parameters: Catalyst: $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$, $n_{\text{catalyst}}/n_{\text{one}}$: 13.3×10^{-4} , reaction time: 20h; reaction temperature: 90 °C, stirring: 1000 rpm and 6 mL of H_2O_2 30 %

Table 1. Reproducibility of the catalytic tests

POMs	-one			-ol/-one		-ene	
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 1	Test 2
$\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$	46	39	41	46	47	21	20
$\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{□}$	30	30	33	34	33	32	31
$\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$	33	32	33	17	17	23	23
$\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$	61	59	59	27	21	11	11
$\text{Cs}_4\text{SbP}_2\text{W}_{12}\text{Mo}_6$	52	48	49	37	34	29	30

Reaction parameters: reaction time: 20 h; reaction temperature: (90 °C for -one and 70 °C for -ene); stirring: 1000 rpm; catalyst/substrate molar ratio: 13.3×10^{-4} and 6 mL of H_2O_2 (30%) added with 0.5 mL/h flow rate using manual mode

in the case of the oxidation of alcohol/ketone and that of alkene to verify the reproducibility of the results. As shown by the results in the Table 1, the AA yields vary very little from one test to another, demonstrating the reproducibility of the catalytic test.

3.2.1 Cyclohexanone oxidation

In order to optimize the reaction parameters favoring to AA formation, the effect of catalyst/substrate molar ratio was examined with $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ catalyst. The cyclohexanone oxidation was carried out at 90 °C, with a fixed flow rate of H_2O_2 of 1 mL every 150 min, a reaction time of 20 h and a magnetic stirring of 1000 rpm. Table 2 shows an increase of AA yield from 12 to 39 % with the increase of catalyst/cyclohexanone molar ratio (noted $n_{\text{catalyst}}/n_{\text{one}}$) from 4.0×10^{-4} to 13.3×10^{-4} . Up to this latter value, AA yield decreases to 32%. For all following catalytic experiments, the catalyst/one molar ratio will fixed at 13.3×10^{-4} , corresponding to 90 mg of catalyst and 15 mmol of substrate.

The effect of H_2O_2 flow rate on the adipic acid formation from cyclohexanone was exam-

Table 2. AA yields as function of catalyst/cyclohexanone molar ratio

$n_{\text{catalyst}} / n_{\text{one}} (10^4)$	AA Yield (%)
4.4	12
6.7	14
8.8	15
9.2	30
13.3	39
18.5	32

Reaction parameters: Catalyst: $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$, reaction time: 20 h, reaction temperature: 90 °C, stirring: 1000 rpm and H_2O_2 30% (8 mL, flow rate: 1 mL/2h30)

ined in the presence $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ catalyst. The oxidation reaction was conducted at 90 °C with a catalyst / cyclohexanone molar ratio of 13.3×10^{-4} , a reaction time of 20 h and a magnetic stirring of 1000 rpm. Hydrogen peroxide (30%) was added during the reaction via a continual automatic mode using a device with a syringe pump that controls the H_2O_2 flow rate (0.2-1.0 mL/h) and a manual mode that consists to add H_2O_2 by fraction of 0.5 or 1 mL/h. For both modes, the injected total H_2O_2 volume is of 6 mL.

Figure 6 shows the obtained results from automatic mode. Two distinct domains were observed, with a maximum of AA yield (52 %), obtained with a flow rate of 0.5 mL/h. From 0.2 to 0.5 mL/h, the AA yield increases from 16 to 52 % and from 0.5 to 1.0 mL/h, it decreases from 52 to 23 %. These results emphasize the hydrogen peroxide flow rate importance on the AA production. So, a low flow rate (<0.5 mL/h), slows down the oxidation reaction of substrate and up to this value (>0.5 mL/h), probably favoured the others oxidation products.

The results of the Table 3 confirms that a H_2O_2 flow rate of 0.5 mL/h leads to best results regardless the used adding mode. So, when

Table 3. Adipic acid yields as function of hydrogen peroxide addition mode and H_2O_2 flow rate

H_2O_2 Flow rate (mL/h)	Mode	AA yield (%)
0.5	Manual	61
	Automatic	52
1	Manual	42
	Automatic	23

Reaction parameters: Catalyst: $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$, $n_{\text{catalyst}}/n_{\text{one}}$: 13.3×10^{-4} , reaction time: 20 h; reaction temperature: 90 °C; stirring: 1000 rpm and 6 mL of H_2O_2 30%

Table 4. AA yields as function of reaction time over $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ and $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ catalyst

POMs	Time (h)	AA yield (%)
$\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$	10	29
	20	39
$\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$	10	28
	20	61

Reaction parameters: reaction temperature: 90 °C, stirring: 1000 rpm; $n_{\text{catalyst}}/n_{\text{one}}$: 13.3×10^{-4} and 6 mL of H_2O_2 (30%) added with 0.5 mL/h flow rate using manual mode

H_2O_2 flow rate increases from 0.5 to 1 mL/h, AA yield decreases from 61 to 42 % for manually adding and from 52 to 23 % for automatically adding. Moreover, regardless H_2O_2 flow rate, the manual mode leads to the highest yields. For the following catalytic tests, a volume of 6 mL of H_2O_2 with a flow rate of 0.5 mL/h and manual addition mode will used.

The time oxidation cyclohexanone effect on AA formation was examined on $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ and $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$. The oxidation reaction was conducted at 90 °C with a catalyst / cyclohexanone molar ratio of 13.3×10^{-4} , a magnetic stirring of 1000 rpm and 6 mL of H_2O_2 (30 %) added with 0.5 mL/h flow rate using manual mode. Table 4 shows that after 10 h of reaction, the AA yields obtained with both POMs are similar (28-29 %), inferior to those obtained after 20 h of reaction (39-61 %) suggesting an active site increase with the reaction time, favoring thus, the AA formation. Whereas, the AA yield increase is more important in the case of $\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$ (from 28 to 61 %) compared to that observed with $\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$ (from 29 to 39 %). These results evidenced the tin action efficiency with the reaction time, on the catalytic performances, lied probably to the presence of redox couples Mo(VI)/Mo(V) and Sn(IV)/Sn(II). This would promote the oxidation either of the substrate or intermediate products to AA.

Table 5 shows the AA yield, obtained from cyclohexanone oxidation, as function of the Dawson-type POM composition. The catalytic performances were investigated under the optimized conditions. The proton total substitution of $\alpha\text{-H}_6\text{P}_2\text{Mo}_6\text{W}_{12}$ heteropolyacid by the different elements (Cs, K, Sb, Sn) favour the adipic

Table 5. AA yields as function of POMs composition and substrate nature

Catalysts	AA Yields (%)	
	-one	-ol(50%) / -one(50%)
$\alpha\text{-H}_6\text{P}_2\text{Mo}_6\text{W}_{12}$	14	—
$\alpha\text{-P}_2\text{W}_{12}\text{Mo}_6$	46	47
$\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{□}$	30	34
$\alpha\text{1-P}_2\text{W}_{12}\text{Mo}_5\text{Sn}$	33	17
$\text{Cs}_4\text{SnP}_2\text{W}_{12}\text{Mo}_6$	61	27
$\text{Cs}_3\text{SbP}_2\text{W}_{12}\text{Mo}_6$	52	37

Reaction parameters: reaction time: 20 h; reaction temperature: 90 °C; stirring: 1000 rpm; catalyst/ substrate molar ratio: 13.3×10^{-4} and 6 mL of H_2O_2 (30%) added with 0.5 mL/h flow rate using manual mode

acid formation with yields of 30-61 % against 14 %. In the case of the potassium based salts series, α -K₆P₂W₁₂Mo₆ is the more active toward AA formation with 46 against 30 and 33 % of yields in the presence of K₁₀P₂W₁₂Mo₅□ and K₈P₂W₁₂Mo₅Sn, respectively. With the caesium based salts series, higher AA yields were obtained (52-61 against 30-46 %). In this series, Cs₄SnP₂W₁₂Mo₆ exhibits the best catalytic performance with an AA yield of 61 %, evidencing the importance of the role played by the tin as counter-ion, results in agreement with those obtained with the Keggin-type POMs [22].

The obtained AA yields (Table 5) from a quimolar mixture, cyclohexanol (-ol) and cyclohexanone (-one) are sensitive to POM composition. In the presence of α -P₂W₁₂Mo₆ and α 1-P₂W₁₂Mo₅□, the alcohol addition to ketone does not seem to influence the formation of AA, thus similar AA yields were obtained, respectively, with 46 and 30% from (-one) oxidation and 47 and 34% from (-ol)/(-one) mixture oxidation. While in the case of α 1-P₂W₁₂Mo₅Sn, Cs₄SnP₂W₁₂Mo₆ and Cs₃SbP₂W₁₂Mo₆, a strong decrease of AA yield from 33 to 17, 61 to 27, and 52 to 37 % was observed, respectively after (-ol) addition to (-one) suggesting that the alcohol inhibits AA formation. This is can be attributed to the hydrogen bonds formation between the C=O group of -one and the hydrogen of C–OH group of -ol, that makes difficult the oxidation of both substrates. Results are in agreement with those observed in literature [12,18-22].

The AA yield increases with oxidative power increase of POM, following sequence: Cs₄SnP₂W₁₂Mo₆ > Cs₃SbP₂W₁₂Mo₆ > α -P₂W₁₂Mo₆ > α 1-P₂W₁₂Mo₅Sn ~ α 1-P₂W₁₂Mo₅□ > α -H₆P₂Mo₆W₁₂. Therefore, these results show that the AA formation requires oxidative sites

Table 6. AA yield as function of POM composition with cyclohexene substrate

Catalysts	Adipic acid yields (%)
α -P ₂ W ₁₂ Mo ₆	21
α 1-P ₂ W ₁₂ Mo ₅ □	32
α 1-P ₂ W ₁₂ Mo ₅ Sn	23
Cs ₄ SnP ₂ W ₁₂ Mo ₆	11
Cs ₃ SbP ₂ W ₁₂ Mo ₆	30

Reaction parameters: reaction temperature: 70°C; reaction time: 20 h; stirring: 1000 rpm; $n_{\text{catalyst}}/n_{\text{-ene}}$: 13.3×10^{-4} and 6 mL of H₂O₂ (30%) added with 0.5 mL/h flow rate using manual mode

coming from the presence several redox couples as Mo(VI) / Mo(V), Sn(IV) / Sn(II), and Sb(V) / Sb(III) and different peroxy-POM species, resulting of hydrogen peroxide action on reduced POM.

3.2.2 Cyclohexene oxidation

The catalytic performances of POMs were examined in the cyclohexene oxidation to adipic acid in the same operation conditions than those used in the cyclohexanone oxidation. The reaction temperature was fixed at 70 °C, temperature inferior to that of boiling point (83 °C). The results of Table 6 show that the POMs are less active in cyclohexene oxidation to AA compared to those obtained from cyclohexanone oxidation with yields of 11-32 % against 30-61%. α 1-P₂W₁₂Mo₅□, and Cs₃SbP₂W₁₂Mo₆ have a similar behaviour with 30 and 32 % of AA yield, superior to those obtained with others catalysts (11-23 %).

Compared to the AA formation from cyclohexanone oxidation that requires of strong oxidative sites, in the case of cyclohexene oxidation, its formation seems to be independent oxidative character of POM. Therefore, a strong oxidative power not favored the cyclohexene oxidation to adipic acid.

The obtained AA yields in this study are inferior to those obtained by others authors with tungsten-based materials [46-52]. Whereas, they used several additives as phase transfer agent, surfactant-type catalysts, organic solvents, ionic liquid and mineral acids, harmful compounds.

3.2.3 Reusability of the catalyst

The catalytic performance of used POM catalyst was also evaluated in order to test its activity as well as its stability. The results are represented in Table 7. Each cycle

Table 7. AA yield (%) obtained from cyclohexanone oxidation with fresh and used POM

POM	AA yield (%) 1 st cycle	AA yield (%) 2 nd cycle
α -P ₂ W ₁₂ Mo ₆	46	0
Cs ₄ SnP ₂ W ₁₂ Mo ₆	61	0
Cs ₃ SbP ₂ W ₁₂ Mo ₆	52	0

Reaction parameters: reaction temperature: 90°C, stirring: 1000 rpm; $n_{\text{catalyst}}/n_{\text{-one}}$: 13.3×10^{-4} and 6 mL of H₂O₂ (30%) added with 0.5 mL/h flow rate using manual mode

lasts 20 h. After recovery of the adipic acid, 15 mmol of cyclohexanone were added to reaction mixture and the oxidation reaction was carried out with the soluble used catalyst, under the optimized conditions. Obtained AA yields after the first run are 46, 61, and 52 % in the presence of α -P₂W₁₂Mo₆, Cs₄SnP₂W₁₂Mo₆, and Cs₃SbP₂W₁₂Mo₆, respectively. When the test was repeated a second one with the same used catalyst, AA was not observed. These results seem to suggest a total deactivation of the catalyst.

4. Conclusion

In this work, the Dawson structure and purity of salt were confirmed by FT-IR and ³¹P NMR spectroscopies, respectively, for potassium salts, α -K₆P₂W₁₈O₆₂, α -K₆P₂W₁₂Mo₆O₆₂, α - α 1-K₁₀P₂W₁₂Mo₅O₆₁, α 1-K₈P₂W₁₂Mo₅SnO₆₁ and cesium mixed salts, Cs₄SnP₂W₁₂Mo₆O₆₂, and Cs₃SbP₂W₁₂Mo₆O₆₂. The UV-Vis spectroscopy showed that tin and antimony based heteropolysalts were partially reduced. The XRD results evidenced the effect of Dawson polyoxometalate composition on its crystalline structure.

The operation conditions of the cyclohexanone oxidation in the presence of 30 % hydrogen peroxide toward adipic acid were optimized. Among, the tested POMs, α -Cs₄SnP₂W₁₂Mo₆O₆₂ and α -Cs₃SbP₂W₁₂Mo₆O₆₂ exhibit the best catalytic performances with 61 and 52 % of adipic acid yield, respectively. In the case of the cyclohexene oxidation, α 1-P₂W₁₂Mo₅O₆₁ and Cs₃SbP₂W₁₂Mo₆ were found to be the most active with 30-32 % of AA yield. The absence of additives as phase transfer agent, organic solvents and mineral acids, in this process makes the synthesis of adipic acid more environments respectful.

Acknowledgement

We thank the financial support by the Ministry of Higher Education and Scientific Research, Algeria.

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