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Cyclohexanone Oxidation to C_4, C_5 and C_6 Dicarboxilic Acids Over P/Mo/W Dawson-Type Polyoxometalates

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Abstract: Polyoxometalates (POMs) are a valuable class of inorganic compounds. The consistency of size and charge of a polyoxometalate structure, together with the inclusion of a variety of transition metals and/or functional groups, has made them very attractive in catalysis and materials science. Dawson and Keggin type POMs are known to be active in the oxidation of cyclohexanone(-One) to C6 dicarboxylic acid, namely adipic acid (AA). In this work, we are interested not only in AA (C6) but also in glutaric GA (C5) and succenic SA(C4) acids. For this purpose, we tested a series of Dawson-type POMs in the oxidation of (-One) at 90°C in the presence of hydrogen peroxide as green oxidant. The catalytic tests were monitored by HPLC during 20 hours of reaction. $K_6P_2W_{12}Mo_6O_{62}$, $K_8P_2W_{12}Mo_5SnO_{61}$ and $Cs_4SnP_2W_{12}Mo_6O_{62}$ were synthesised, characterised then tested in the oxidation of cyclohexanone to dicarboxylic acids (C4, C5 and C6). The obtained results show that the formation of these products depends not only on the reaction time but also on the chemical composition of the catalyst. So, GA is favoured after 4 hours of reaction in the presence of $K_8P_2W_{12}Mo_5SnO_{61}$ with 59.11 10^{-4} mol. The highest amount of SA was obtained after 4 hours of reaction over 26.32 10^{-4} mol of $Cs_4SnP_2W_{12}Mo_6O_{62}$ as catalytic system. In addition, using the same catalyst, the progression of the reaction over time led to an increase in the amount of AA. Since, after 20 hours, 30.47 10^{-4} moles of AA were obtained compared to 1.07 and 1.19 10^{-4} moles of C5 and C4 diacids respectively. At the last we can concluted that the P/Mo/W Dawson POMs catalyst is a promising alternative for the synthesis of dicarboxylic acids from cyclohexanone in the presence of hydrogen peroxide.

Keywords: Dawson polyoxometallate, Adipic acid, Succenic, Glutaric, Cyclohexaone, Hydrogene peroxide

Introduction

Polyoxometallates (POMs) are metal-oxide clusters, presenting a great diversity of structure (Li et al., 2007) among them, those of Dawson structure with metal (M: Mo, W...)/heteroatom (X:P, Si....) ratio equal to 9. These POMs are a crystalline network made of heteropolyanions (HPA) of general formula $[X_2M_{18}O_{62}]^{n-}$, counter ions (H^+, K^+, Cs^+,...) and water molecules. Heteropolyanions are composed of an arrangement of 18 octahedrons whose center is a transition metal ion 'M(VI)' and the vertices are oxygen. These octahedrons are arranged in a particular form around a tetrahedron constituted by the heteroatom X and whose vertices are oxygen atoms in

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common with those of the octahedrons (Guerroudj et al., 2019). The diversity of the chemical composition of these compounds offers greater flexibility on their acid (Bronsted & Lewis, 1923) and redox properties (Briand et al., 2003; Contant et al., 2007). Dawson-type POMs have been shown to be effective in various oxidation catalytic processes (Moudjahed et al., 2013).

In this work, we report the cyclohexanone oxidation to dicarboxylic acids as C4, C5 and C6, among them adipic acid, C6, which is an important product principally used in nylon synthesis. But the industrial process of its production uses an excess of HNO_3 (60-70%) which generates a large amount of greenhouse gases, as N_2O, the most dangerous one (Thiemens et al., 1991). The development of a clean alternative to this process was already the subject of several of our previous works (Amitouche et al., 2018; Mouanni et al., 2019; Gureoudj et al., 2019). On the other hand, recent study has shown that Keggin based tin POMs promotes AA synthesis (Maiouf et al, 2022). So, the objective of this work is to examine catalytic activity of Dawson-type POMs (α1-$K_8P_2W_{12}Mo_5SnO_{62,}$ α-$Cs_4SnP_2W_{12}Mo_6O_{62}$ and α-$K_6P_2Mo_6W_{12}O_{62}$) in C4-C6 synthesis from cyclohexanone in the presence of hydrogen peroxide (30 %) without solvent. POMs were characterized by IR, ^{31}P NMR and UV–Vis spectroscopies and X-ray diffraction.

Experimental

Materials Synthesis

The 1,4,9,10,15,16-$K_6P_2W_{12}Mo_6O_{62}$ and 1,9,10,15,16-4-$K_8P_2W_{12}Mo_5SnO_{61}$ (noted α1-$P_2W_{12}Mo_6$ and α1-$P_2W_{12}Mo_5Sn$) were synthesized from hexavacant anion $[H_2P_2W_{12}\square_6O_{48}]^{12-}$ according to established procedures (Harmalker et al., 1983; Randal et al., 1996). The mixed cesium salt of formula $Cs_4SnP_2W_{12}Mo_6O_{62}$ (noted $CsSnP_2W_{12}Mo_6$) has been prepared by precipitation from α-$H_6P_2W_{12}Mo_6O_{62}$, $SnCl_2$ or $SbCl_3$, and CsCl according with the stoichiometric ratios. Figure1. schematizes and illustrates the preparation steps of these polyoxometallates.

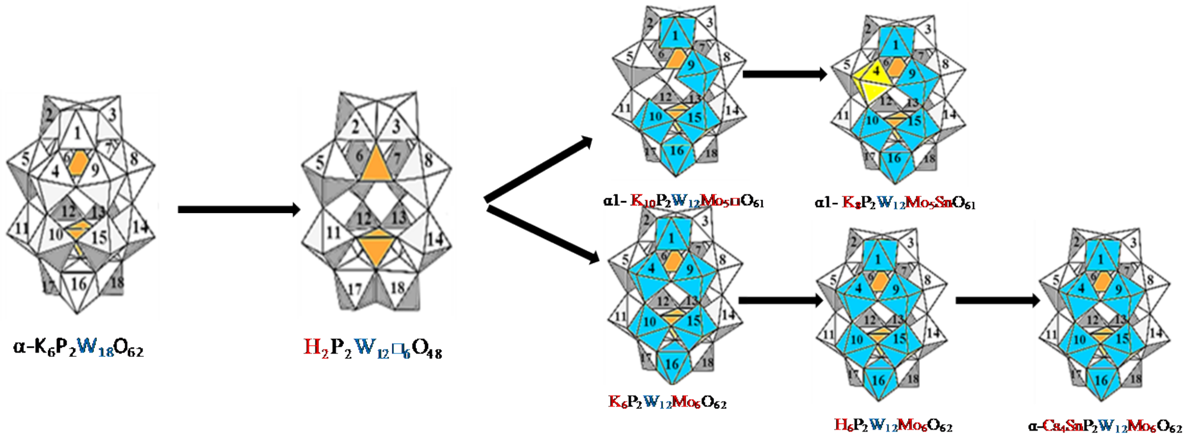

Figure 1. Preparation steps of these polyoxometallates

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 and ^{31}P MAS NMR spectra were measured at room temperature on Bruker Avance 400 spectrometer. The 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 and theX-ray Diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu-Kα (k = 1.54178 Å) radiation, in the range of 2θ = 5-60° at a rate of 0.02 $°.s^{-1}$.

Dicarboxylic Acids Synthesis

The dicarboxylic acids synthesis method is like that already used for AA production (Tahar et al., 2014) it is that described by ((Nomiya et al., 1984). Then, the oxidation of cyclohexanone was carried out under reflux condenser at 90°C using a 100 L round bottomed flask equipped with a magnetic stirring bar. The reaction medium composition was as follows: -One, catalyst and H_2O_2 (30%) was stirred at 1000 rpm for 20h reaction time.

Adipic acid, one of the oxidation products, was isolated as crystals and identified by FT-IR spectroscopy and melting point (152 ˚C). The quantification of the other products, glutaric and succinic diacids, were quantified was performed by HPLC.

Results and Discussion

Materials Characterization

FTIR Spectroscopy

Figure 2 shows the FT-IR spectra of $P_2W_{12}Mo_6$, $P_2W_{12}Mo_5Sn$ and $CsSnP_2W_{12}Mo_6$. The IR vibrational bands, characteristic of the different phosphorus-oxygen and metal-oxygen bonds in the Dawson heteropolyanion structure (Figure 3.), were observed for all the prepared POMs in the short wavelength region (500 -1100 cm^{-1}). In addition to these bands, $P_2W_{12}Mo_5Sn$ exhibits another band at 1140 resulting from the loss of symmetry attributed to the presence of Sn instead of Mo. This is the consequence of the bursting of the (P-Oa) band at around the Sn site.

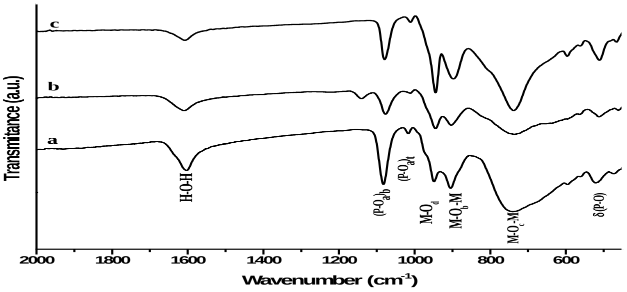

Figure 2. FT-IR spectra of (a) $P_2W_{12}Mo_6$, (b) $P_2W_{12}Mo_5Sn$ (c) and $CsSnP_2W_{12}Mo_6$

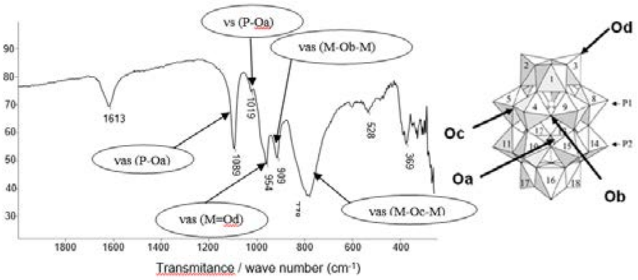

Figure 3. FT-IR spectrum of $K_6P_2W_{12}Mo_6O_{62}$

^{31}P NMR Spectroscopy

Figure 4 shows ^{31}P NMR spectra of all the prepared POMs. The results of this analysis demonstrate that α-$P_2W_{12}Mo_6$ (b) and $Cs_4SnP_2W_{12}Mo_6$ (f) present a single chemical shift, which confirms the symmetry and purity of these heteropolyanions. The ^{31}P NMR result of $P_2W_{12}Mo_5Sn$ (Figure 4. e) shows two different chemical shifts at - 8,9 and - 11,1 ppm. This result is to be expected, in the case of non-symmetrical POMs, knowing that the chemical environment of the two phosphors (P1 and P2) of this POM is different. Indeed, the top half is distinct from the bottom one of POM.

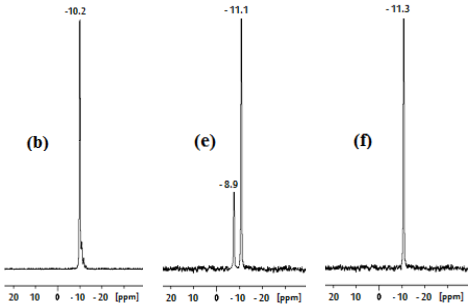

Figure 4. ^{31}P NMR spectra of α-$P_2W_{12}Mo_6$ (b), $K_7P_2W_{12}Mo_5Sn$ (e) and $Cs_4SnP_2W_{12}Mo_6$ (f)

UV-Vis Spectroscopy

The diffuse reflection UV-visible spectra of the heteropoly compounds $P_2W_{12}Mo_6$ (Figure 5.), $P_2W_{12}Mo_5Sn$ (c) and $Cs_4SnP_2W_{12}Mo_6$ (d) (Figure 6.) show a large band in the wavelength range 200-500 nm, assigned to oxygen-metal charge transfer (LMCT), corresponding to the oxidation state VI of metal. It' s characteristic of metal-oxygen (M(IV)-O) charge transfer (M= W and Mo) (Cavani et al., 2001; Dermeche et al., 2012).

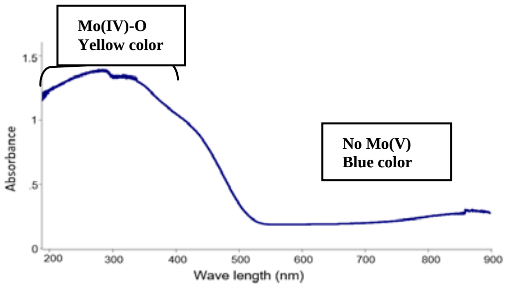

Figure 5. UV-visible spectrum of $K_6P_2W_{12}Mo_6O_{62}$

The introduction of Sn in the POM structure leads to the appearance of another TCLM band around 700 nm which can be attributed to the V oxidation state of the metal. This result suggests the partial reduction of POM confirmed by the blue color attributed to the presence of Mo(V) observed during its preparation, it highlights that an electron exchange takes place between Sn(II) and Mo (VI) according to the following equations:

$$Sn^{2+} + 2Mo^{6+} \Leftrightarrow Sn^{4+} + 2Mo^{5+}$$

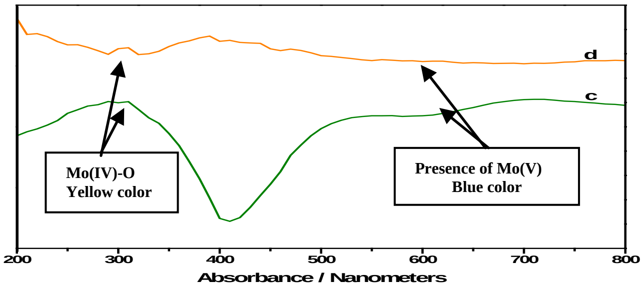

Figure 6. UV–Vis spectra of $Cs_4SnP_2W_{12}Mo_6$ (c) and $LiK_9P_2W_{12}Mo_5Sn$ (d)

X-ray Diffraction

Figure 7 shows the results of X-ray patterns of $P_2W_{12}Mo_6$, $P_2W_{12}Mo_5Sn$ and $CsSnP_2W_{12}Mo_6$. The diffractogram (b) of $P_2W_{12}Mo_6$ shows that this POM crystallizes in a triclinic system with the appearance of some additional lines observed at 2θ values of 45.64; 49.4; 51.68; 53.16 and 54.76. The processing software indicates a crystallinity rate of 99.63% and proposes to us mesh parameters similar to those of $K_6P_2W_{18}O_{62}$ (ICSD: 2310827) having the lattice parameters a= 12.8600 Å, b= 14.8300 Å, c= 22.3400 Å, α= 94.400°, β= 116.870°, γ= 115.600° and a space group P $\bar{1}$ (2) (Dawson et al., 1953).

The X-ray patterns of the tin-containing POMs Figure 7. b ($CsSnP_2W_{12}Mo_6$) and c ($P_2W_{12}Mo_5Sn$)) show very similar 2θ values, with a slight difference in the intensity of the lines. The processing software proposes for both salts the monoclinic system with different mesh parameters. In the case of the $CsSnP_2W_{12}Mo_6$ salt, these parameters are a= 20.42600 Ǻ, b= 11.85400 Ǻ, c= 24.81100, α= γ= 90°, β=97.060° and a space group P 1 21/c 1 (14). In the case of $P_2W_{12}Mo_5Sn$ salt, the corresponding mesh parameters are a= 7.1765 Ǻ, b= 9.2874 Ǻ, c= 5.2968 Ǻ, α= γ= 90°, β=106.034° with a space group P 1 21/n 1 (14).

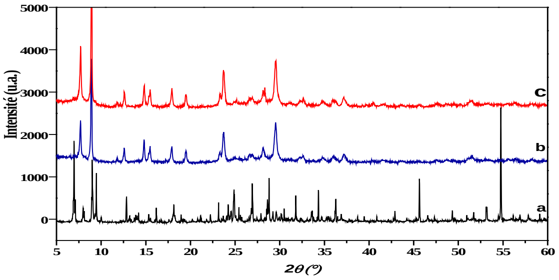

Figure 7. XRD patterns of (a) $P_2W_{12}Mo_6$ (a) $P_2W_{12}Mo_5Sn$ (b) $CsSnP_2W_{12}Mo_6$ (c)

Cyclohexanone Oxidation to C6, C5 and C6 Dicarboxilic Acids

The catalytic activity of $P_2W_{12}Mo_6O_{62}$, $P_2W_{12}Mo_5Sn$ and $CsSnP_2W_{12}Mo_6$ were examined in cyclohexanone oxidation to C6, C5 and C4 dicarboxilic acids namely adipic (AA), succinic (SA) and glutaric (GA) acid respectively. The effects of the chemical composition of the polyoxometalate and the reaction time were examined at 90°C using peroxide of hydrogen as oxidant.

Adipic Acid Yield as Function of Catalyst Composition

Table 1 shows the AA yields obtained from the oxidation reaction of cyclohexanone using the 03 polyoxometalates as catalysts. The catalytic performances were evaluated under the optimized conditions (catalyst/substrate molar ratio: 13.2 10^{-4}, total volume of H_2O_2 (30%): 6ml, H_2O_2 flow rate: 0.5ml/h).

Table 1. AA yields as function of catalyst composition

Polyoxométallate (catalyst)	Notation	AA Yield (%)
1, 4, 9, 10, 15, 16-$K_6P_2Mo_6W_{12}O_{62}$	$P_2W_{12}Mo_6$	47
1, 9, 10, 15, 16-4 $K_8P_2W_{12}Mo_5SnO_{61}$	$P_2W_{12}Mo_5Sn$	33
1, 4, 9, 10, 15, 16-$Cs_4SnP_2W_{12}Mo_6O_{62}$	$CsSnP_2W_{12}Mo_6$	61

The results show that $CsSnP_2W_{12}Mo_6$ is the most efficient catalyst with AA yields of 61, from the oxidation of cyclohexanone. The yields vary according to the following sequence:

$$CsSnP_2W_{12}Mo_6\,(61\%) > P_2W_{12}Mo_6\,(47\%) > P_2W_{12}Mo_5Sn\,(33\%)$$

The low yield observed in the presence of $P_2W_{12}Mo_5Sn$ compared to other POMs is probably related to the asymmetry of this POM and its instability.

Adipic, Succeni and Glutaric Acid Evolution as a Function of Catalyst Composition and Reaction Time

Figure 8 and Table 2 show the evolution as a function of time of cyclohexanone conversion and adipic, succinic and glutaric acids selectivity, in the presence of $P_2W_{12}Mo_6$, $CsSnP_2W_{12}Mo_6$ and $P_2W_{12}Mo_5Sn$. The formation of these products depends on the reaction time and the chemical composition of the catalyst. According to the obtained results, GA (C5) is favoured after 4 hours of reaction in the presence of $K_8P_2W_{12}Mo_5SnO_{61}$ as catalyst with 59.11 10^{-4} mol. The highest amount of SA (C4) was obtained after 4 hours of reaction with $Cs_4SnP_2W_{12}Mo_6O_{62}$ (26.32 10^{-4} mol). Using the same catalyst, the reaction progression over time led to an increase in the amount of AA(C6) in favor of the other products (after 20 hours, 30.47 10^{-4} mol of adipic acid were obtained against 1.07 and 1.19 10^{-4} mol of C5 and C4 diacids respectively).

According to the curves shown in Figure 8(A), the conversion of cyclohexanone reaches 96% after 4h of reaction and is total after 8h. The formation of the diacids SA, GA and AA evolves to reach a maximum of 10.43 10^{-4}, 10.14 10^{-4} and 15.85 10^{-4} moles respectively after 20h of reaction. We note the progressive formation of AA and SA from 4h to 20h of reaction while GA is at its highest value (17.3 10-4 moles) at 8h of reaction where it's the most formed compared to AA (12.58 10^{-4} moles).

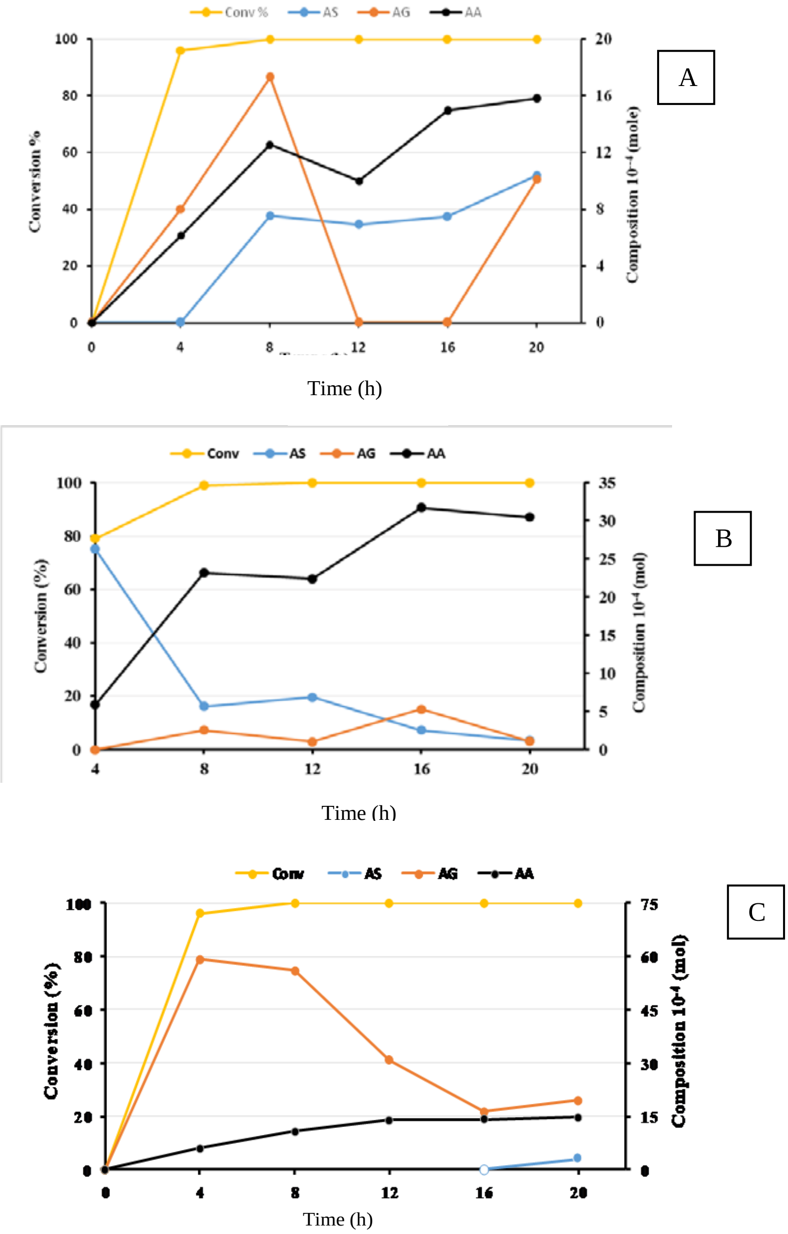

Figure 7. Time course of the conversion and selectivities of the oxidation products of cyclohexanone in the presence of (A) $P_2W_{12}Mo_6$, (B) $CsSnP_2W_{12}Mo_6$ and (C) $P_2W_{12}Mo_5Sn$

Comparative Study

Table. 3 summarizes all the results including the conversion rate of cyclohexanone, the molar composition of SA, GA and AA diacids with selectivity, obtained for each sample carried out at 4, 8, 12, 16 and 20h of reaction. $P_2W_{12}Mo_6$ is very active with conversions of 96-100%. The product distribution is strongly influenced by the reaction time. Thus, with a time of 4 and 8 h, the catalyst is selective in GA with 56 and 46% respectively and in AA with 43 and 33% respectively. While after 12 and 16 h of reaction time, $P_2W_{12}Mo_6$ becomes selective in AA with 59 and 66% selectivity respectively and in SA with 40 and 53% selectivity respectively. After 20h of reaction, AA is the product with 43% selectivity and succinic and glutaric acids were obtained with selectivities of the same order of magnitude (27-29%).

$P_2W_{12}Mo_5Sn$ is as active as other POMs with conversions of 95-100% and also very selective in GA whatever the reaction time with 52-90% against 52-90% against 9-46% selectivity in AA. SA was only observed after 20h of reaction with only 8% selectivity. The table shows that AA is the major product in the presence of $CsSnP_2W_{12}Mo_6$ with 93% of selectivity after 20h of reaction. On the other hand, GA is the most formed one t in the presence of $P_2W_{12}Mo_5Sn$ with 90% selectivity after 4h of reaction. $CsSnP_2W_{12}Mo_6$ is also selective to SA with 81% selectivity after 4h of reaction. The examination of these results shows that high selectivities (69-93%) in AA, GA and SA were obtained depending on the time and the nature of the catalyst highlighting the importance of these parameters in the distribution of the products of the cyclohexanone oxidation

Table 3. Conversion (Conv), molar composition (C.M) and selectivity (S) of products as a function of reaction time

POM	Time	Conv (%)	SA C. M (10^4)	S (%)	GA C. M (10^4)	S (%)	AA C. M (10^4)	S (%)
$P_2W_{12}Mo_6$	4	96	0	0	8.04	56	6.16	43
	8	100	7.56	20	17.3	46	12.58	33
	12	100	6.92	40	0	0	10.01	59
	16	100	7.53	53	0	0	14.98	66
	20	100	10.43	29	10.14	27	15.85	43
$P_2W_{12}Mo_5Sn$	4	95	0	0	59.11	90	06	9
	8	100	0	0	56.03	83	10.75	16
	12	100	0	0	30.76	68	13.88	31
	16	100	0	0	16.34	53	14.03	46
	20	100	2.98	8	19.38	52	14.68	39
$CsSnP_2W_{12}Mo_6$	4	79	26.32	81	0	0	5.9	18
	8	99	5.69	18	2.53	8	23.19	73
	12	100	6.86	22	1.03	3	22.42	74
	16	100	2.52	6	5.31	13	31.75	80
	20	100	1.19	3	1.07	3	30.47	93

Conclusion

The characterization results of the as prepared polyoxometallates ($K_6P_2W_{12}Mo_6O_{62}$, $K_8P_2W_{12}Mo_5SnO_{61}$ and $Cs_4SnP_2W_{12}Mo_6O_{62}$ show by FTIR that they have the characteristic vibration bands of the Dawson anion. The ^{31}P NMR confirmed the purities and the Dawson-type structure. UV-Visible spectroscopy revealed that the tin substituted POMs are partially reduced. The XRD analysis demonstrated that the crystal structure depends on the chemical composition of the POM. The reactivity of these polyoxometallates catalysts in carboxylic acids synthesis from cycloexanone shows that $Cs_4SnP_2W_{12}Mo_6O_{62}$ is the most active with a yield of 61%. The observed results of HPLC analysis showing the evolution over time of the conversion of cyclohexanone and the formation of reaction products shows that the distribution of the products depends on the nature of the catalyst and the reaction time. All POMs are very active with a conversion of cyclohexanone in the order of 100%.

Adipic diacid is the main product in the presence of $Cs_4SnP_2W_{12}Mo_6O_{62}$ (**93%** selectivity) after 20h of reaction time. The Glutaric diacid is favoured in presence of $K_8P_2W_{12}Mo_5SnO_{61}$ (**90% s**electivity) after 4h of reaction time and the Succinic one is the main product in the presence of $Cs_4SnP_2W_{12}Mo_6O_{62}$ **(81%** selectivity) after 4h of reaction. Finally, we can conclude that P/Mo/W Dawson POMs catalysts are a promising alternative to carboxylic diacids synthesis from cyclohexanone in presence of hydrogen peroxide

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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