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Tin-Based Keggin-Type Phosphomolybdate and Silicomolybdate as Catalysts for the Green Synthesis of Adipic Acid

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Abstract: The catalytic activity of two series of Keggin-type salts of formula $Cs_{4-x}Sn_xSiMo_{12}O_{40}$ (x: 0.5 and 1) and $Cs_{3-x}Sn_xPMo_{12}O_{40}$ (x: 0.25-1) was examined in the liquid phase cyclohexanone oxidation to adipic acid (AA) in the solvent absence. The materials were prepared and characterized by FTIR, UV-Vis and SEM. The adipic acid synthesis was carried out at 90°C in presence of hydrogen peroxide (30%), a green oxidant that produces only water as by-product. The effects of catalyst/substrate molar ratios and time reaction on dipic acid yields were studied. The results of this study showed that the POM-H_2O_2 system was found to be efficient for the production of adipic acid from the oxidation of cyclohexanone and the yields were closely dependent on the operating conditions. The highest AA yield (55%) was obtained with $Cs_2Sn_{0.5}PMo_{12}O_{40}$ using a catalyst/substrate molar ratio of 3.7×10^{-3} and a reaction time of 20h.

Keywords: Adipic acid, Phosphomolybdates, Silicomolybdates, Keggin-type, Cesium-tin salts.

Introduction

In recent decades, the use of Keggin-type polyoxometalates (POMs) as catalysts and photocatalysts in various types of reactions has developed very rapidly (Mizuno et al., 2006). These POMs are composed of a heteropolyanion of the general formula $[XM_{12}O_{40}]^{n-}$, made up of metal oxide groups containing transition metals in high oxidation states (M : W(VI), Mo(VI)... and X : Si(IV), P(V)...) (Pope et al., 1983) and a counter-ion which can be a proton, an organic group, a metal (alkaline, alkaline-earth, transition) and/or a non-metal. Their particularity resides in the structural and electronic characteristics and the acidic (Lewis and/or Bronsted) and redox properties (Mizuno et al., 2009). They also have the advantage of being able to undergo rapid and reversible redox transformations under mild conditions. In addition, the redox and acid properties of POMs can be adjusted according to the heteropolyanion composition and the counter-ion nature, making it possible to develop an effective strategy for a multifunctional catalysis (Mazari et al., 2013; Mouheb et al., 2018).

In this context, we chose to study two series of POMs with compositions $Cs_{4-x}Sn_xSiMo_{12}O_{40}$ (x: 0.5 and 1) and $Cs_{3-x}Sn_xPMo_{12}O_{40}$ (x: 0.25-1). These materials, prepared and characterised by several techniques, were tested in the oxidation of cyclohexanone to adipic acid (C_6 diacid) with the aim of examining the influence of their composition on their catalytic properties.

C_6 diacid is one of the most widely synthesised products in industry. It is mainly used as a precursor in the synthesis of nylon-6, polyamide 6 and other food and cosmetic products. The industrial process uses concentrated nitric acid as oxidant in the oxidation of both cyclohexanone and cyclohexanol, in the presence of

a Cu/V catalyst. In addition to the formation of adipic acid, this process also causes the formation of nitrogen oxides (NOx), in particular nitrous oxide (N_2O), which contributes to the destruction of the ozone layer and the greenhouse effect.

To overcome these drawbacks, several alternatives have been proposed for the adipic acid synthesis. Among these, the POM-H_2O_2 based system appears to be a promising alternative to the industrial process, as it is a non-polluting process. Unlike HNO_3, H_2O_2 produces only water as a by-product.

The POM-H_2O_2 system was first used by Nomiya et al. (1984) in the cyclohexanone oxidation to adipic acid. Many studies have subsequently been based on this system, using POMs of different compositions to improve the yield of adipic acid (Cavani et al., 2011; Idrissou et al., 2018., Tahar et al., 2015; Mazari et al., 2013; Benadji et al.,2013; Mouanni et al., 2018; Mouanni et al., 2019; Mouheb et al., 2018; Moudjahed et al., 2016; Guerroudj et al., 2019; Moudjahed et al., 2022).

Previous research has highlighted the effectiveness of Keggin and Dawson type POMs in the cyclohexanone oxidation to adipic acid, particularly those based on tin, antimony and cobalt. This performance was attributed to the presence of redox couples (Sn(IV)/Sn(II), Sb(V)/Sb(III) and Co(III)/Co(II)) and Mo(VI)/Mo(V), which favour the oxidation-reduction process.
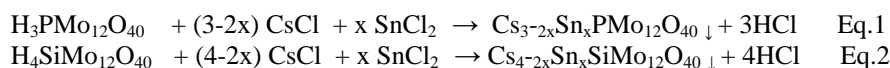
In this work, the catalytic properties of two series of Keggin-type salts of formula $Cs_{4-x}Sn_xSiMo_{12}O_{40}$ (x: 0.5 and 1) and $Cs_{3-x}Sn_xPMo_{12}O_{40}$ (x: 0.25-1) were studied in the liquid phase oxidation of cyclohexanone to adipic acid (AA) at 90°C in the presence of hydrogen peroxide (30%) without solvent, with the aim of examining the effect of the heteroatom (P and Si) on the yield of adipic acid. The materials were prepared and characterised by FTIR, UV-Vis and SEM.

Experimental

Polyoxometalates Synthesis

$H_3PMo_{12}O_{40}.13H_2O$ and $H_4SiPMo_{12}O_{40}.14H_2O$, heteropolyacids, were prepared by the conventional method described in the literature (Copeaux et al.,1909; H. Copeaux et al., 1907; Rocchicioli-Deltcheff et al., 1976; Sanchez et al., 1982).

$Cs_{3-2x}Sn_xPMo_{12}$ (x: 0.25-1) and $Cs_{4-2x}Sn_xSiMo_{12}$ (x: 0.5 and 1), heteropolysalts were synthesized from the, $H_3PMo_{12}O_{40}$ and $H_4SiPMo_{12}O_{40}$ heteropolyacids, respectively, via cation exchange by adding of caesium and tin chlorides according to the stoichiometric coefficients (Eqs. 1 and Eqs. 2), as described in an earlier works (Mouheb et al., 2020).

$$H_3PMo_{12}O_{40} + (3\text{-}2x)\, CsCl + x\, SnCl_2 \rightarrow Cs_{3-2x}Sn_xPMo_{12}O_{40} \downarrow + 3HCl \qquad Eq.1$$
$$H_4SiMo_{12}O_{40} + (4\text{-}2x)\, CsCl + x\, SnCl_2 \rightarrow Cs_{4-2x}Sn_xSiMo_{12}O_{40} \downarrow + 4HCl \qquad Eq.2$$

Characterization

- – Infrared spectroscopy was recorded on a Shimadzu IR Afdinity- 1S spectrometer.
- – UV–Vis spectra were performed at room temperature on Thermo scientific Evolution 220 spectrometer between 200 and 800 nm.
- – The SEM images were recorded on a Philips microscope Environmental ESEM X l30.

Catalytic Test

The liquid-phase oxidation of cyclohexanone was carried out at 90°C using a 100 mL round-bottomed flask under reflux according to method described by Nomiya et al. (Nomiya et al.,1984) as detailed in our previous studies (Mouheb et al., 2018; Mouanni et al., 2019; Mouheb et al.,2020). The catalytic oxidation of the substrate to adipic acid is closely controlled by the POM-H_2O_2 system. Hydrogen peroxide feeds this catalytic system by providing oxygen via the POM, which oxidizes the cyclohexanone to the diacid. The oxidant, H_2O_2, thus enables the POM to regenerate, according to the mechanism illustrated in the scheme in Figure 1.

$$POM_{ox}\,(Mo^{VI}) + Substrate \rightarrow POM_{red}\,(Mo^{V}\ and\ Mo^{VI}) + Product$$
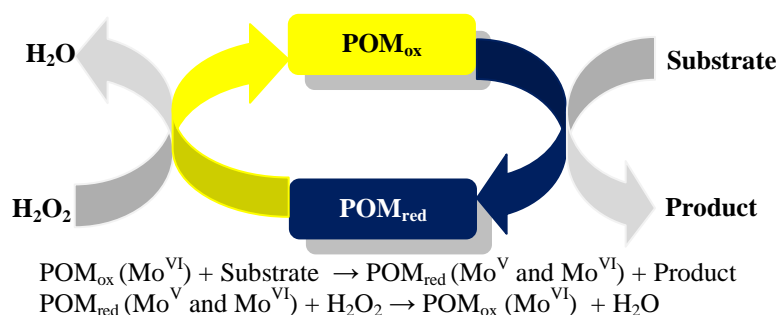$$POM_{red}\,(Mo^{V}\ and\ Mo^{VI}) + H_2O_2 \rightarrow POM_{ox}\,(Mo^{VI})\ + H_2O$$

Figure 1. Catalytic cyclohexanone oxidation principle in the presence of POM-H_2O_2 system

Keggin-type phosphomolybdates and silicomolybdates have a yellow colour, characteristic of molybdenum in the degree of oxidation (VI). After oxidation of the substrate, the reduced POM takes on a blue colour, characteristic of Mo (V). The addition of hydrogen peroxide drop by drop, each time the POM is reduced, restores the yellow colour of the POM, demonstrating the regeneration of the POM. Visualising the change in the oxidation state of the Mo by the change in colour helps to preserve the efficiency of the POM by maintaining the oxidising properties in each catalytic cycle until the substrate is exhausted. It should be noted that only two Mo (VI) atoms per Keggin anion can undergo reduction at any one time. The resulting homogeneous reaction mixture was cooled to 0°C overnight. Adipic acid (AA), one of the oxidation products, is the only one that can be isolated in the form of white crystals. AA is identified by HPLC chromatography and FTIR spectroscopy (Figure 2) . Its melting point is (~151°C). AA yield was calculated as follows:

$$AA\ yield\ (\%) = AA\ recovered\ mass \times 100\ /\ theoretical\ AA\ mass$$
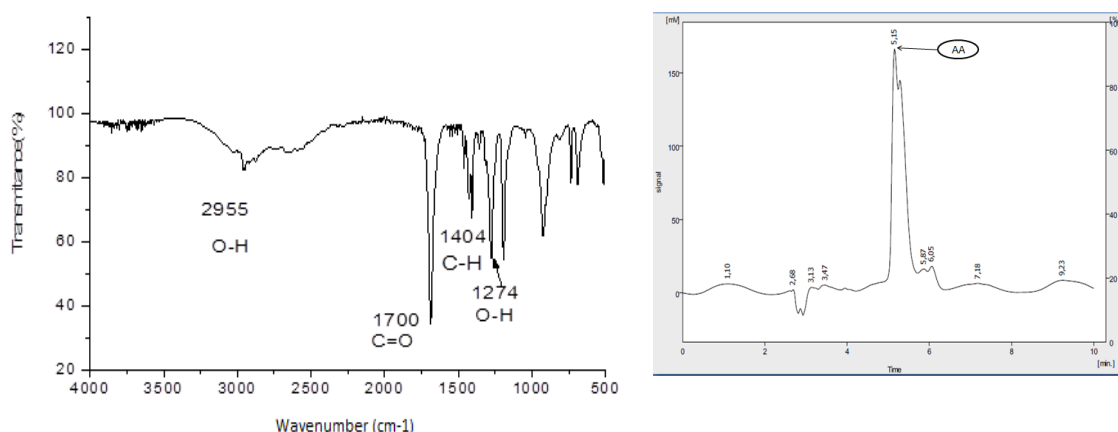

Figure 2. FTIR spectra and HPLC chromatogram of obtained adipic acid

Results and Discussion
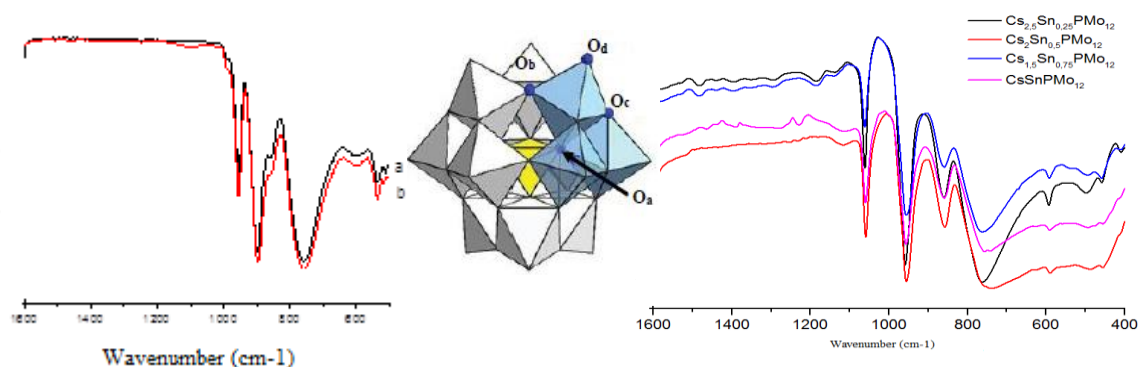
Characterization

Figure 3. FT-IR spectra of (a): $Cs_2Sn_1SiMo_{12}O_{40}$, (b) $Cs_3Sn_{0,5}SiMo_{12}O_{40}$ and $Cs_{3-2x}Sn_xPMo_{12}O_{40}$ series

FTIR spectra (Figure 3) of prepared POMs have the characteristic vibration bands of the Keggin anion in the 1100-500 cm^{-1} spectral range (Rocchiccioli-Deltcheff et al., 1983) related to 4 oxygen types Oa, Ob, Oc and Od. These bands are located at 1060-1066cm^{-1}, 951-970cm^{-1}, 869-890cm^{-1} and 760-810cm^{-1} corresponding to ν_{as} (P-Oa), ν_{as} (M-Od), ν_{as} (M-Ob-M) and ν_{as} (M-Oc-M) respectively. Nevertheless, silicomolybdic salts (figure 3) $Cs_2Sn_1SiMo_{12}O_{40}$ and $Cs_3Sn_{0.5}SiMo_{12}O_{40,}$ show a weak intensity of the Si-Oa band at around 1000 cm^{-1} and a shoulder at around 850cm^{-1} with shift in the vibration band, as obtained in parent heteropolyacid spectrum. This change in vibration frequency probably corresponds to a symmetry defect in the Keggin anion. The FTIR results showed that the structure of the Keggin anion is not affected by Cs and Sn proton substitution.

The UV-Vis spectra of $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ (Figure 4) show a broad metal-oxygen charge transfer (MOCT) band in the 200-500nm region made up of three components linked to the three types of oxygen Ob, Oc and Od of Keggin anion, a UV-Vis spectrum typical of a Keggin structure corresponding to a VI oxidation state of molybdenum. (Guerroudj et al., 2019). In addition to this band, another band around 700nm, attributed to the presence of molybdenum in an oxidation state (V), appears in the UV-Vis spectra of tin-substituted POMs. This result is justified by the dark blue colour of the tin-based salts, characteristic of the presence of Mo (V), in agreement with data from the literature (Dermeche et al., 2009). These results suggest that tin-containing POMs are partially reduced, which can be explained by the exchange of electrons between Sn(II) and Mo(VI) according to the following equation:
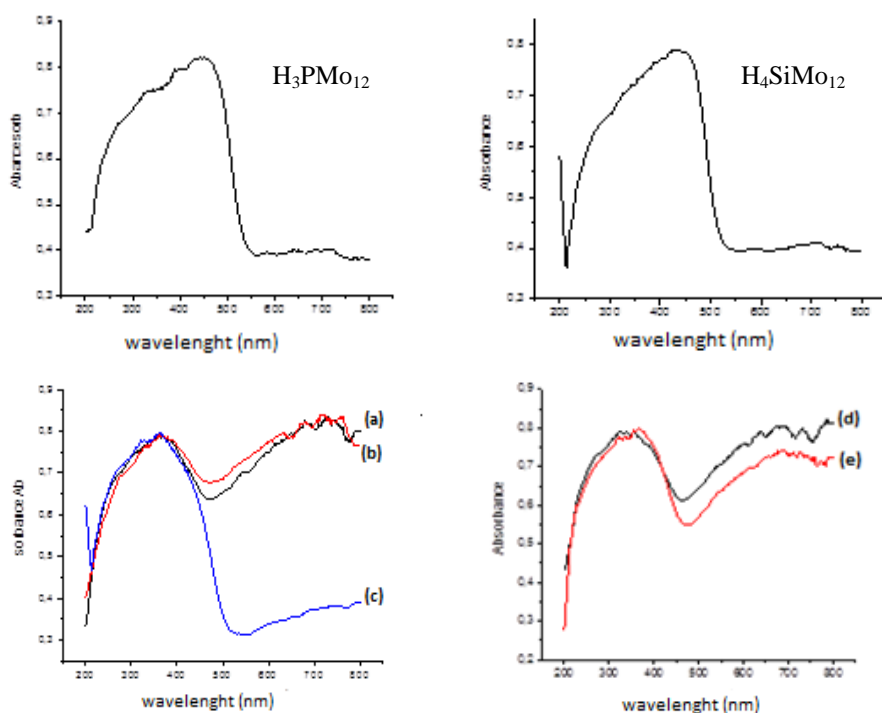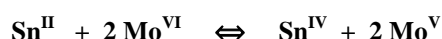
$$Sn^{II} + 2 Mo^{VI} \Leftrightarrow Sn^{IV} + 2 Mo^{V}$$

Figure 4. UV-Vis spectra of the two Keggin-type heteropolyacids, (a): $Cs_2Sn_{0.5}PMo_{12}$, (b): $CsSnPMo_{12}$, (c): $Cs_3PMo_{12}O_{40}$, (d): $Cs_3Sn_{0.5}SiMo_{12}$ and (e): $Cs_2SnSiMo_{12}$
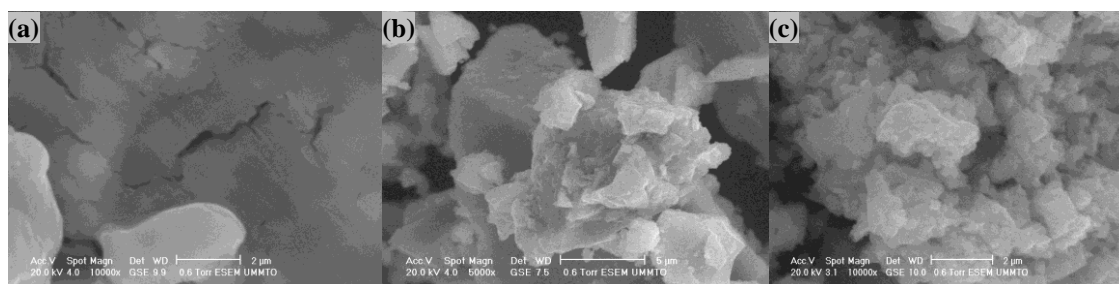
Figure 5. SEM images of (a): H3PMo12O40, (b): Cs1Sn1PMo12O40 and (c) Cs2Sn0,5PMo12O40

In order to compare the morphology of the catalysts, a SEM analysis was performed on $H_3PMo_{12}O_{40}$, $Cs_1Sn_1PMo_{12}$ and $Cs_2Sn_{0.5}PMo_{12}$. SEM images of $H_3PMo_{12}O_{40}$, $Cs_1Sn_1PMo_{12}O_{40}$ and $Cs_2Sn_{0.5}PMo_{12}O_{40}$ show a

POM morphology that is very sensitive to their chemical composition (Figure 5). The tin-based salts show a denser structure composed of small spherical particles compared with the $H_3PMo_{12}O_{40}$ morphology. On the other hand, an increase in the density of spherical particles is observed with increasing Sn content (this is clear from images (b) and (c) in Figure 5).

Cyclohexanone Oxidation

Table 1 displays the obtained AA yields, under the used operating conditions for the cyclohexanone oxidation (catalyst/substrate molar ratio = 10^{-3}), as a function of the chemical composition of the catalyst. The two acids $H_4SiMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ have higher AA yields than those obtained with the salts (26 versus 16-24%). Among the salts, $Cs_3Sn_{0.5}SiMo_{12}O_{40}$ and $Cs_2Sn_{0.5}PMo_{12}O_{40}$ are more effective at forming adipic acid than $Cs_1Sn_1PMo_{12}O_{40}$ and $Cs_2Sn_1SiMo_{12}O_{40}$ with AA yields of 23-24 against 16-20%. The AA yield obtained with 0.5 atoms of Sn per Keggin unit, similar to that obtained with the two heteropolyacids, may be explained by the fact that the Bronsted acidity may be equivalent to the Lewis acidity introduced by the SnIV/SnII couple following electron exchange with Mo(VI) (Mouheb et al., 2020).

Table 1. AA yield as a function of chemical composition of catalyst.

Phosphomolybdates			Silycomolybdates		
Catalyst	AA yield (%)	$Tf_{AA}*(°C)$	Catalyst	AA yield (%)	$Tf_{AA}*(°C)$
H_3PMo_{12}	26	151	H_4SiMo_{12}	26	148
$Cs_2Sn_{0.5}PMo_{12}$	24	152	$Cs_3Sn_{0.5}SiMo_{12}$	23	152
$Cs_1Sn_1PMo_{12}$	16	151	$Cs_2Sn_1SiMo_{12}$	20	150

Reaction conditions : $n_{catalyst}/n_{-one} = 10^{-3}$; T=90°C ; t=20h ; agitation rate: 1000 rpm, H_2O_2 30%.

On the basis of the previous results (Guerroudj et al., 2019) and in order to improve the efficiency of the catalysts, a study of the variation catalyst/substrate molar ratio was carried out with $Cs_2Sn_{0.5}PMo_{12}O_{40}$ and $Cs_3Sn_{0.5}SiMo_{12}O_{40}$. The results (Figure 6 (A)) reveal that, the AA yield has increased from 16 to 40% and from 11 to 29% when the catalyst/substrate molar ratio increased from 0.50×10^{-3} to 1.83×10^{-3}, in the presence of $Cs_2Sn_{0.5}PMo_{12}O_{40}$ and $Cs_3Sn_{0.5}SiMo_{12}O_{40}$, respectively. This result shows that the cyclohexanone oxidation to adipic acid is very sensitive to catalyst/substrate molar ratio. This is probably due to increase of active sites.

In order to further investigate the influence of the catalyst/substrate molar ratio on AA performance, the best performing catalyst $Cs_2Sn_{0.5}PMo_{12}O_{40}$, was selected to examine this parameter (Figure 6 (B)). The results show a similar AA yield 21 and 27% for extreme ratios 1.0×10^{-3} and 4.7×10^{-3}, respectively and similar AA yield 40-46% for intermediate ratios 1.33×10^{-3} - 2.70×10^{-3}. It should be noted that the highest yield (55%) is obtained with a ratio of 3.70×10^{-3}. It can be seen that the yield of adipic acid is very sensitive to the catalyst/substrate molar ratio.
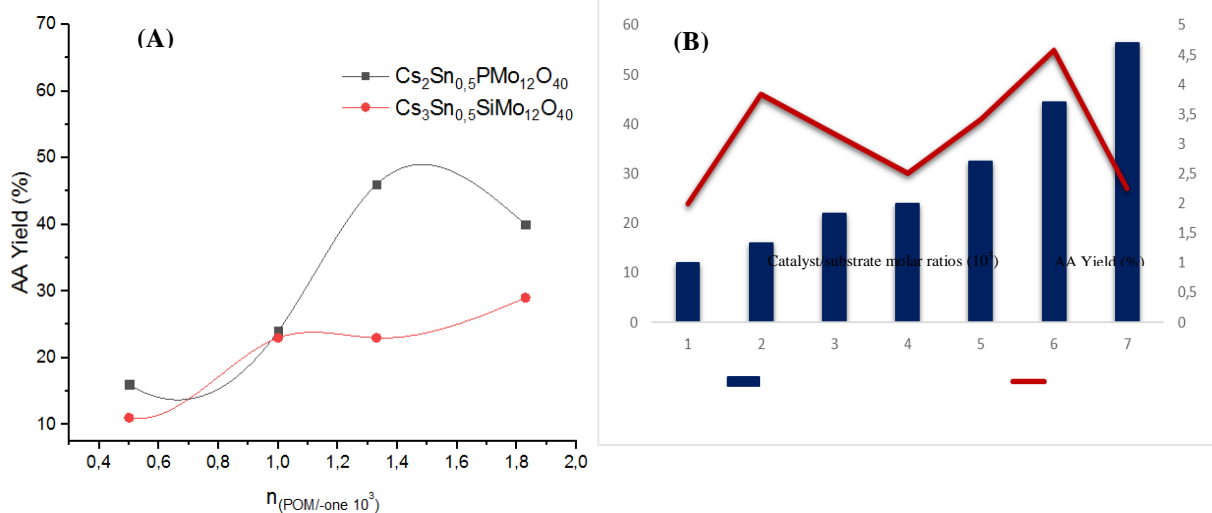

Figure 6. Evolution of AA yield as a function of the catalyst/substrate molar ratio: (A) comparative study between $Cs_2Sn_{0.5}PMo_{12}O_{40}$ and $Cs_2Sn_{0.5}SiMo_{12}O_{40}$. (B) $Cs_2Sn_{0.5}PMo_{12}O_{40}$

Table 2 shows the effect of tin steochiometric coefficient 'x' from the $Cs_{3-2x}Sn_xPMo_{12}O_{40}$ series (x: 0.25-1) on AA yields. The oxidation of cyclohexanone was carried out with an optimised catalyst/cyclohexanone molar ratio of 3.7×10^{-3} .The results show that an increase in tin atoms per Keggin unit from 0.25 to 0.5 led to an increase in AA yield from 31 to 55%. For values of x greater than 0.5, the AA yield decreases from 55% to 40-41% and subsequently appears to be independent of the value of x. These results show that the best formulation for obtaining the highest yield (55%) is $Cs_2Sn_{0.5}PMo_{12}O_{40}$.

Table 2. Adipic acid yields as a function of the Sn atoms number in $Cs_{3-2x}Sn_xPMo_{12}O_{40}$

Catalyst	Adipic acid Yields (%)
$Cs_{2.5}Sn_{0.25}PMo_{12}O_{40}$	31
$Cs_2Sn_{0.5}PMo_{12}O_{40}$	55
$Cs_{1.5}Sn_{0.75}PMo_{12}O_{40}$	40
$CsSnPMo_{12}O_{40}$	41

Reaction conditions: $n_{catalyst}/n_{-one} = 3.7 \times 10^{-3}$, T°=90°C, agitation rate :1000rpm,H_2O_2 30%.

Figure 7 illustrates the evolution of adipic acid yield as a function of reaction time in the presence of optimized catalyst $Cs_2Sn_{0.5}PMo_{12}O_{40}$ and under optimum conditions. The formation of adipic acid increases with reaction time, so the yield increases from 22 to 55% after 20h of reaction This result suggests that a time of 20 h is necessary to achieve the maximum AA yield, result in agreement with those reported in previous work which demonstrated a conversion of intermediates to adipic acid with time (Mouheb et al.,2020).
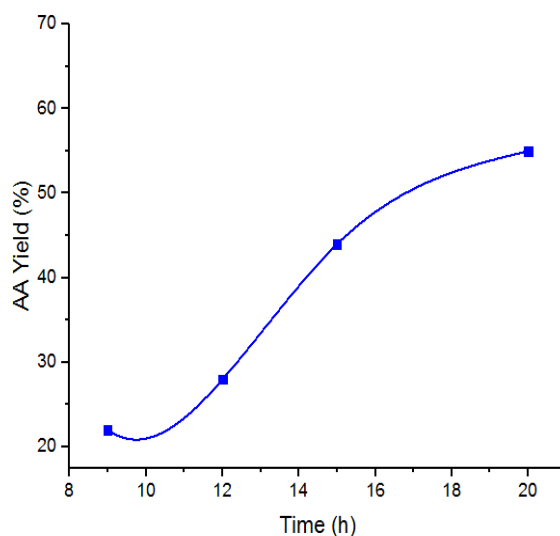

Figure 7. adipic acid yield as a function of reaction time.
Reaction conditions : $n_{catalyst}/n_{-one} = 3.7 \times 10^{-3}$, T°=90°C, agitation rate :1000rpm,H_2O_2 30%.

Conclusion

The non-soluble salts prepared, $Cs_{4-x}Sn_xSiMo_{12}O_{40}$ (x: 0.5 and 1) and $Cs_{3-x}Sn_xPMo_{12}O_{40}$ (x: 0.25-1) series well-characterised have a Keggin-type structure in a partially reduced state with the simultaneous presence of Mo(VI)/ Mo(V) and Sn(IV)/ Sn(II). Their morphology is particularly sensitive to chemical composition. Both series showed good catalytic activity, depending on the catalyst/substrate molar ratio, in the liquid phase cyclohexanone oxidation to adipic acid. The reaction was carried out without solvent and in the presence of hydrogen peroxide (30%). Among the different POMs, $Cs_2Sn_{0.5}PMo_{12}O_{40}$ was the most efficient with a 55% of adipic acid yield. The absence of solvent, a harmful product, and the use of hydrogen peroxide, that decomposes only into water, make the POM-H_2O_2 system clean.

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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